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SEPARATION OF INHOMOGENEITIES IN BOTTLE GLASS BY DENSITY DIFFERENCES*

By John C. Turnbull

Abstract

Cordy glass consisting of a mixture of fibers or laminations of various glasses of slightly differing compositions is separated in the form of powder by differences of density. These differences in general run parallel with differences of thermal expansion which produce the polariscopic appearance of cordiness. The separated fractions can be analyzed chemically, and therefore, perhaps, for the first time an estimate can be made of the chemical errors involved in the cords of the old polariscopic gradings, A, B, C. The most important features of the technique are (1) the elimination of moisture from the glass and the suspending liquid and (2) the use of a special centrifuge with accurate control of temperature.

I. Introduction

The chemical and physical properties of inhomogeneities or cords, consisting of glassy inclusions in glass, are difficult to evaluate while they remain in the matrix glass. Cords in bottle glass are observed with a polariscope which detects the permanent stress associated with the cord. Optical glass is examined for inhomogeneities in refractive index, and very minute variations can be found. In either case, however, the irregular structure of the cords makes comparisons or absolute measurements difficult. Evidence of chemical inhomogeneity may be found by etching glass either with hydrofluoric acid or alkalis, as cords may consist of glass more or less resistant than the matrix glass. Reactions involving base exchange, such as silver staining, will sometimes act differentially on the cord.[1]

It is difficult, however, to find anything of a quantitative nature about the inhomogeneity by these means, and the desirability of removing the inhomogeneity from the matrix glass is evident. This has been done by using the density differences between the cord and the matrix glass.

The method consists essentially of powdering the glass and suspending it in a dense liquid, whose density is adjusted so that the least dense particles will float and the most dense particles will sink. A centrifuge is used, for otherwise the separations would be quite slow with fine particles.

This method is now being applied to the study of cords in bottle glass. After a separation of the cordy glass has been made, it is possible to measure some of the chemical and physical differences between the cordy glass and the matrix glass. Samples large enough for chemical analysis can be obtained, and the composition differences for moderately bad cords are usually large enough that they can be measured by analysis. Differences in refractive index, thermal coefficient of expansion, and other physical properties can be measured on the separated fractions.

* Presented at the Autumn Meeting, Glass Division, Hershey, Pa., September 6, 1940. Received September 19, 1940.

[1] J. C. Turnbull and W. A. Weyl, "Staining Glasses with Silver: Possibility of Studying Inhomogeneities," *Glass Ind.*, **21** [1] 13–18 (1940).

II. Apparatus and Method

The success of the method depends on the removal of water from the glass powder and from the liquid in which it is suspended. The density of the glass particles is changed by adsorption of water, which is proportional to surface area, but, unless water is removed, the separation tends to be made on the basis of surface-area differences rather than of density differences. The magnitude of the density change caused by adsorption may be quite large. From pycnometer measurements of the density of feldspars, Day and Allen[2] reported a lowering of density of 0.006 gm. per cc. for powders less than 150-mesh in size before heating to remove air and water adsorbed during grinding. Water films also cause solids, which are suspended in liquids immiscible with water, to stick together or to flocculate. Changes in sedimentation volume of 200% or greater, owing to saturation with water, have thus been observed in suspensions of glass spheres from 5 to 15 microns in diameter in immiscible liquids.[3] This flocculation, of course, makes any separation difficult, for it is essential that the particles should be able to move independently of each other. The procedure described here has been developed to permit the removal of water which has been adsorbed by the particles and dissolved in the organic liquids used to suspend the powders.

(1) Procedure

The glass is powdered in a diamond mortar and screened to a size between 0.002 and 0.006 inch, the value depending on the nature of the cord being investigated. Fine material is removed by suspension in methyl alcohol, leaving a powder of fairly uniform particle size. The dry powder is then placed in a Pyrex-brand tube and outgassed in a vacuum furnace, the heat treatment being for 3 hours at 525°C. in a vacuum of the order of 0.01 mm. of Hg. This treatment should get rid of all films except those of monomolecular dimensions whose effect on density is negligible. The temperature (525°C.) is higher than necessary because there

[2] A. L. Day and E. T. Allen, "Isomorphism and Thermal Properties of Feldspars," *Carnegie Inst. Wash. Pub.*, No. 31 (1905); *Amer. Jour. Sci.*, [4] **169** [19] 93–143 (1905).

[3] C. R. Bloomquist and R. S. Shutt, "Fine Particle Suspensions in Organic Liquids," *Ind. Eng. Chem.*, **32** [6] 827–31 (1940).

is some evidence that most of the water is removed at temperatures near 250°C.

Figure 1*a* shows the shape of the Pyrex-brand tube in which the powder is outgassed and later put through the centrifuge. The lower constriction, placed about half way between the top and bottom of the suspending liquid, prevents the mixing of the separated fractions, which might occur either during the time the centrifuge is being stopped and the tube is being examined or while the fractions are being removed from the tube. The upper constriction permits sealing off the tube under vacuum (Fig. 1*b*).

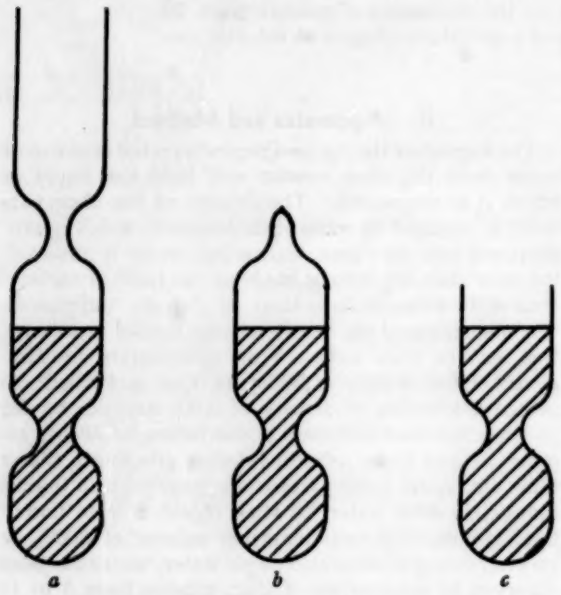

FIG. 1.—Shapes of Pyrex-brand tubes used in the centrifuge; tube *a* is sealed off under vacuum at upper constriction, giving tube *b*; tube *c* is sealed with a rubber or neoprene stopper.

After outgassing, the tube is cooled at atmospheric pressure in a desiccator. The composition of the heavy liquid in which the powder is to be suspended, a mixture of *s*-tetrabromoethane and isopropyl salicylate (density 3 and 0.9 gm. per cc., respectively), is adjusted so that its density is equal to the average density of the powder at 35°C. This can be done by suspending in the liquid a large piece of the glass from which the powder has been prepared and by changing its density by adding one or the other of the component liquids. This liquid, in a suitable container, is evacuated to 0.01 mm. of Hg and is heated to 100°C. in order to remove the dissolved air and water from it, the vaporizing liquid being refluxed back into the container. Isopropyl salicylate is used as the light liquid because it has about the same vapor pressure as the heavy liquid; if some substance, such as acetone, having a much different vapor pressure were used, the composition and density of the mixture would change during refluxing because of loss of the component of higher vapor pressure.

Both the powder and the liquid are now sufficiently free of water, the liquid is transferred in air to the tube containing the powder, and the tube is evacuated again and heated to 100°C. The second evacuation removes the air from around the powder and also whatever water has been taken up by the liquid during transfer. While the tube is under vacuum, it is sealed off at the upper constriction, leaving the suspension permanently under vacuum and protected from the atmosphere.

A tube of the shape shown in Fig. 1*c* is used for some of the separations, and a rubber stopper is inserted instead of sealing off the tube. This is less satisfactory because the seal is not so good, the suspension is not under vacuum, and a slow reaction takes place between the rubber stopper and the heavy liquid. If, however, the powder has a large density spread, the separations can be carried out well enough, and this tube is somewhat more convenient and rapid.

The relative density of the liquid to the glass powder must be changed within small limits during a separation. This is done by changing its temperature, inasmuch as the temperature coefficient of density of the liquid is about 0.002 gm. per cc. per degree C. It follows also, as variations in density of the order of 0.001 gm. per cc. are observed for bottle glass, that the temperature should be held constant to 0.1° (or better).

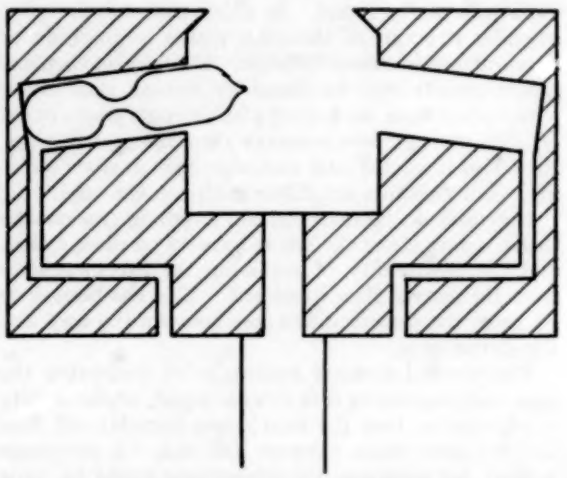

FIG. 2.—Cross section of centrifuge head. One Pyrex-brand tube is shown in position. A stream of water of constant temperature enters the head from above along its axis, flows past the Pyrex-brand tube and is discharged at the lower surface of the head.

The temperature of the suspension therefore is controlled by running water of constant temperature through the centrifuge head. The head (Fig. 2) is machined from a Dow metal casting and is mounted directly on a $^3/_4$-h.p. series wound motor. Water, flowing by gravity from a 10-gallon tank, enters the head and flows directly past the tube containing the suspension. It leaves the lower surface of the head at a point about $1^1/_2$ in. from the axis of the centrifuge and is pumped back into the tank. One-half gallon of water can be circulated per minute, and its temperature, regulated by a mercury thermoregulator to 0.02°C., can be adjusted anywhere in the range between 25° and 55°C.

III. Measurements on Separated Fractions

One indication of the inhomogeneity of the glass is the density spread among the particles of the powder. This is defined as the temperature range over which the density of the liquid, determined by its temperature, lies between the densities of the least and most dense particles. In this temperature range, therefore, a separation of the powder is observed after centrifuging, the light particles going to the top of the suspending liquid and the heavy ones to the bottom. The corresponding density spread of the glass particles can be found by calculation from the temperature coefficient of density of the liquid.

Routine measurements have been made of the density spread for glass taken from the regular production of a glass container manufacturer. Over a period of several months (except for one week in May), two bottles were taken each week from each of three tanks. Two ring sections were cut from the barrel of each bottle; one was examined in the polariscope, and the cord rating was determined on the scale given by Swicker[4] for ring sections. The other was powdered, and the density spread was determined for particles from 150- to 200-mesh in size. These results are shown in Fig. 3.

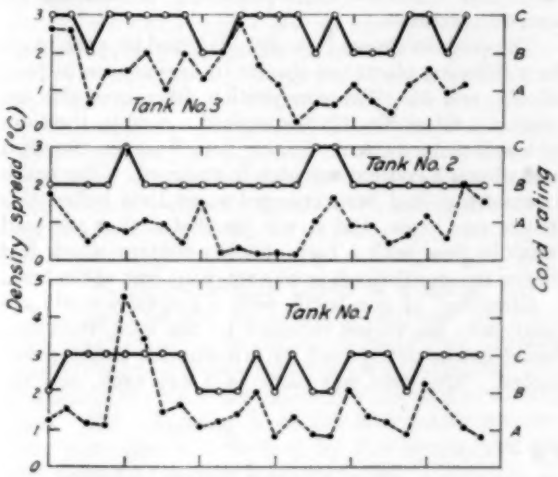

FIG. 3.—Density spread, measured twice weekly, for normal production of a glass container plant over a period of several months; the polariscopic cord rating is shown in solid lines.

From these data, the average density spread for bottles having a polariscopic cord rating of B was found to be 1.0°C., or 0.002 gm. per cc.; and for C cords, 1.6°C., or 0.003 gm. per cc. There is thus a rough correlation between the Swicker rating and the density spread. In particular cases, however, this correlation is not accurate (see Fig. 3); for example, there are many C glasses having less density spread than some B glasses in this group.

This result is not unexpected as the polariscopic ratings are made partly on the basis of distribution of cord, of which the density separation takes no account. Other things being equal, a fine cord is rated better than a heavy cord polariscopically, although in either case the composition difference and density spread might be the same. It is possible, too, that composition differences might be found which would cause a large change in the thermal coefficient of expansion and therefore high stress in the cordy glass without causing a large change in density.

Variations in glass composition for the glass made by this company, resulting from variations in batch composition, can be checked on the tape from the recording scales. Over a period of 24 hours, maximum variations were as large as 0.4% of SiO_2, 0.2% of Na_2O, and 0.1% of CaO and MgO; variations three fourths as large as these were frequent Using the density factors given by English and Turner,[5] the maximum variations in density computed for these composition variations are of the order of 0.004 gm. per cc., or 2°C. Batch variations then evidently are sufficient to explain the density differences observed with this glass and also the moderate cord present in some of the production.

IV. Chemical Analysis

Cords, worse than grade B, usually have a density spread greater than 1°C., which will be shown to be well above the limit of sensitivity of the separation technique. Separations have been made for a number of cordy glasses, some of grade C and some worse, in order to measure by chemical analysis the composition differences between matrix glass and cords.

Approximately 1.5 gm. of powder are taken for these separations, using the centrifuge tube which, after the water is removed, is sealed off by a rubber stopper. The temperature is adjusted so that about 200 mg. of the densest particles go to the bottom in the centrifuge and the remainder float. The less dense particles are removed by pouring into another similar tube the liquid and lighter particles, leaving behind the denser particles which are packed on the bottom of the first tube. The temperature for the second tube is raised until 200 mg. of the lightest particles are floating; these are removed in a similar manner. This gives three fractions on which a chemical analysis can be run.

Ghering[6] has modified the standard methods of analysis for application to these samples, which are roughly one tenth the size used in the standard methods, and he has contributed the results for about 20 different cords which were separated and analyzed. Some idea of the accuracy of the work may be obtained from Table I, which shows results over a period of two months for the Bureau of Standards standard sample No. 128; Na_2O, CaO, MgO, and R_2O_3 were determined directly, other minor constituents were not determined, and silica was found by difference in most cases. The compositions given are accurate to about 0.1% for Na_2O, CaO, and R_2O_3; until

[4] V. C. Swicker, "Ring-Section Examination of Glass Containers," *Bull. Amer. Ceram. Soc.*, **18** [4] 143–47 (1939).

[5] S. English and W. E. S. Turner, "Density of Soda-Lime-Magnesia Glasses and Calculation of Density," *Jour. Soc. Glass Tech.*, **6**, 228–31 (1922); *Ceram. Abs.*, **2** [10] 219 (1923).

[6] L. G. Ghering of Preston Laboratories.

recently, the determination of MgO was not so satisfactory, and this is the least reliable figure in the results given here. Variations in determinations on other homogeneous glasses in Table I are of the same order of magnitude. For separated glasses, the separation itself is another variable, and, as the results for glass No. 43 show (Table I), variations in analyses are larger for separated fractions than for homogeneous glasses.

TABLE I

REPRODUCIBILITY OF CHEMICAL ANALYSIS

(200-mg. samples)

	Standard sample No. 128					
Na_2O	16.67	16.75	16.72	16.82	16.79	16.80
R_2O_3	1.98	1.91	1.96	1.93	2.03	1.98
CaO	4.80	4.75	4.72	4.75	4.73	4.73
MgO	3.20				3.32	3.32

	Other homogeneous glasses		
	No. 131	No. 51	No. 1213
Na_2O	15.37	15.81	15.51
	15.35	15.71	15.43
R_2O_3	2.21	1.45	2.58
	2.27	1.59	2.47
CaO	7.09	5.72	10.72
	7.13	5.81	10.82
MgO	1.29	4.07	
	1.31	4.05	

	Separated fractions of glass No. 43		
	Dense	Intermediate	Light
Na_2O	16.09	15.91	15.39
	16.00	16.08	15.34
	15.98	15.80	15.27
R_2O_3	1.25	1.28	1.43
	1.29	1.34	1.31
	1.24	1.31	1.26
CaO	7.36	7.48	6.82
	7.47	7.24	6.77
	7.51	7.35	6.85
MgO	2.26	1.96	1.91
	2.06	1.91	2.04
		2.10	

Table II is a summary of the results for several different cordy glasses, which gives the differences in composition between the most dense and the least dense fractions, a positive figure indicating an increase in concentration from the dense to the light fraction. Most of the changes in composition are well above the experimental limits of analysis.

Glasses Nos. 91, 61, and 51 are bottles made on the same tank within a period of two months. The cord in each case consists of a streak down the side wall of the bottle and across the base. The cord could be separated with a glass cutter from the homogeneous part of the bottle; if this were done, however, the differences in composition would be about one third the difference obtained by the method described. The matrix glass, which was quite homogeneous, had the same density (within $^1/_5°$, or 0.0004 gm. per cc.) as the heavy fraction, and the compositions were the same within experimental error. The cords, therefore, are represented by the light fractions. The high silica content of the cord indicates that it may have been caused by batch segregation, by solution of silica refractory floating in the tank, or possibly by foreign cullet. It is quite probable in this case that the cord was not caused by solution of aluminous refractory because the increase in silica of more than 1% is not accompanied by a substantial increase in alumina.

The cords in glasses Nos. 391, 131, and 50, each made in a different plant, are similar in appearance to Nos. 91, 61, and 51. The composition differences also are similar. Glass No. 1213 contained a cord in the form of a well-defined streak; in this case, however, the silica and alumina content are high in the cord. The batch composition had been changed some time before this bottle was made, and it was concluded that the cord was old glass with a high alumina content which had begun to come through from a stagnant part of the tank.

Glass No. 43 is a bottle with a generally cordy appearance; the region occupied by the cord, therefore, could not be determined by examination in the polariscope. The glass was made in a day tank, and the

TABLE II

SUMMARIZED RESULTS

	No. 91	No. 51	No. 61	No. 391	No. 131	No. 1213	No. 43	No. 1251	No. 50	No. 60
SiO_2	2.30	1.35	1.25	0.78	0.94	0.40	1.40	2.23	0.99	0.22
Na_2O	−0.80	−0.45	−0.40	−0.38	−0.42	−0.49	−0.67	−0.78	−0.81	−0.15
R_2O_3	−0.02	0.05	−0.05	−0.05	−0.05	0.60	0.11	0.39	−0.01	0.00
CaO	−0.78	−0.60	−0.50	−0.30	−0.40	−0.51	−0.64	−1.84	−0.11	−0.02
MgO	−0.70	−0.35	−0.30	−0.06	−0.07		−0.20		−0.06	−0.05
ΔD	0.013	0.010	0.010	0.008	0.006	0.004	0.013	0.013	0.009	0.001
	0.041	0.023	0.023	0.014	0.012	0.005	0.020	0.031	0.013	0.002
$\Delta D'$	0.025	0.014	0.014	0.009	0.010	0.009	0.016	0.020	0.010	0.002
$\Delta\lambda$ ($\times 10^7$)	−4.0	−2.4	−2.1	−1.7	−2.0	−2.3	−3.2	−4.8	−3.0	−0.6
Thermal-shock strength*	Spontaneous breakage	80°	No spontaneous breakage	95°	Spontaneous breakage					100°

The composition differences given refer to the cord and the matrix glass, that is, the heavy and light fractions. Opposite ΔD are the minimum and maximum density differences obtained in the centrifuge for the particles in the light and heavy fractions; $\Delta D'$ gives the density differences (calculated from the English and Turner factors[6]) from the observed composition differences; $\Delta\lambda$ is the difference in expansion coefficient calculated from the composition differences.

* Temperature for initial breakage, A.S.T.M. thermal-shock test for glass containers.

cord, which may have been caused by batch variations, was observed on starting up the tank. The cord in glass No. 1251, a rolled flat glass is known to be caused by batch segregation of which high change in lime is characteristic. The cord was so bad that the glass could not be cut.

The density spread was determined for these glasses before making the separations. The minimum density difference between particles in the two fractions, given by the difference in the temperatures at which the light and heavy fractions were separated, was found in the course of the separations. The average density difference between the two fractions in Table II (computed from the composition differences using factors given by English and Turner[5]) will be seen, with only one exception, to lie between these maximum and minimum density differences.

The average difference in thermal-expansion coefficient between the cord and matrix glass, or between the light and heavy fractions, can be calculated roughly (from similar factors) from the differences in composition described. This figure is given in Table II, together with the thermal-shock strength of the bottles, which is also a measure of cord severity or differences in thermal-expansion coefficient. Spontaneous breakage on the worst of these cordy glasses was observed several days or months after the bottles were formed; and the bottles showing this breakage have the largest differences in composition, density, and computed thermal-expansion coefficient. The cords with the lowest composition differences, in general, caused the least trouble. Glass No. 60, which appeared to be very cordy in the polariscope, showed practically no composition difference or density spread; it also had a satisfactory thermal-shock strength.

V. Experimental Limits of Method

In order to find the least density difference for which particles of glass can be separated, some work has been done with optical glass which has density variations several orders of magnitude less than those found in bottle glass. The outgassing procedure and sample preparations were also standardized by this means, and the best speed for the centrifuge was found.

The appearance of the powder in the Pyrex-brand tube after a run in the centrifuge will reveal whether or not a separation has been made. If the density of the liquid is not close to that of the powder, the particles quickly rise or fall in the tube; and at the end of the run, the liquid appears clear, and the particles are massed together at one end of the tube. For the finer powders at 3000 r.p.m., the liquid becomes clear in about 15 minutes or less, depending on how close the liquid density is to that of the glass. The particles pack firmly in the absence of water and vigorous shaking is necessary to redistribute them through the liquid. As the liquid density approaches that of the powder, the packing becomes less firm; for a short temperature range with optical glass, the powder goes neither to the top nor to the bottom but remains uniformly distributed through the liquid. The difference between the lowest temperature, for which the powder is packed at the bottom of the tube, and the highest temperature, for which it is packed at the top of the tube, is taken as the effective limit of separation.

For powders of optical glass, ground to pass 200-mesh and not 325-mesh (0.002 to 0.003 in.), the limit of separation, obtained in this way at a centrifuge speed of 3000 r.p.m., is 0.2°C., which corresponds to a density difference of 0.0004 gm. per cc. For powders with particles differing by more than 0.0004 gm. per cc. in density, a separation would be obtained over a certain range of temperature, and the powder in this temperature range would be driven to both ends of the tube in the centrifuge. These results show that the foregoing procedure is adequate to remove water from the powder.

The main interference with the separation of very fine particles is the change in density and flocculation produced by adsorbed material. Another difficulty, which also limits the method, arises from the compressibility of the heavy organic liquid. Thus, while the suspension is being centrifuged at high speeds and large accelerations, the weight of the heavy liquid itself produces a high pressure on the bottom of the tube containing the suspension. This pressure increases the density of liquid at the bottom of the tube, but it has no effect on the density of liquid at the top of the tube. Table III shows the acceleration, the pressure on the bottom of the tube, and the corresponding density difference between the top and bottom of the heavy liquid for a number of centrifuge speeds calculated for a compressibility of the mixture of isopropyl salicylate and tetrabromoethane of 10^{-4} change in unit volume per atmosphere. This figure is of the order of the compressibility for liquids such as bromoform, which resemble tetrabromoethane chemically.

The speed of the centrifuge is the limiting factor for separation with optical glass. If the temperature is set at the lowest value for which the powder packs at the bottom of the tube (e.g., at 3000 r.p.m.) and if the centrifuge is run at double this speed, the powder will no longer pack at the bottom but will remain suspended through the liquid. The effect, however, is somewhat smaller than the figures indicate. Thus, the limit of separation at a speed of 3000 r.p.m., as determined with optical glass, was 0.0004 gm. per cc., which is less than the computed figure of 0.0006 gm. per cc. (Table III).

VI. Degree of Separation Obtained with Inhomogeneous Powders

By microscopic examination of the separated fractions, it is possible to tell whether a separation according to density differences has really been effected. If much water is present, all of the small particles will occur in the light fractions and the large ones in the dense fraction, and in this case, of course, no real separation has been made.

If water is removed, the effectiveness of the separation can be determined from the index of refraction of the particles in the two end fractions. Using monochromatic light and varying the index of an immersion liquid by variations in the temperature of the micro-

scope stage, the index of the immersion liquid is made equal to that of one of the fractions. The particles of this index then disappear, and particles of different index, belonging to the other fraction, do not.

TABLE III

Speed (r.p.m.)	Acceleration* (gm.)	Pressure difference in centrifuge tube (atmospheres)	Density change in heavy liquid (gm./cc.)
14,000	15,000	56	14 × 10^{-3}
10,000	7,500	28	7 " "
5,000	1,900	7	1.8 " "
3,000	675	2.5	0.63 " "
1,000	75	0.28	0.07 " "
500	19	0.07	0.02 " "

* Radial acceleration is $a = 0.0026\ N^2$ ft./sec.^{2} Centrifuge factor is $a/g = 0.0026\ N^2/32$.

Index differences of about 0.001 occur between the two end fractions for powders having a density spread of more than 4°C., or 0.008 gm. per cc. In these cases, the separations are good, and less than 10% of the particles in either of the end fractions are so different in density that they appear not to belong to that fraction. There seems to be little tendency for particles of one fraction to be locked into the wrong fraction by the packing of other particles.

Separations made for powders of less density spread than 2° are hard to check in this way because the index differences are slight. A bottle glass, made just after changing a tank from green to amber with no change in composition other than that in coloring materials, was observed to have a density spread of only 0.4°C., or 0.0008 gm. per cc. The glass, chiefly amber with a streak of green, showed slight stress in the polariscope. The two end fractions obtained by density separation, however, were found to have a substantial difference of color after they were melted down at 1400°C., the light fraction being colorless (the amber color was removed by oxidation) and the dense fraction a pale green. Evidently the separation in the green glass was quite good, as it went largely to the denser fraction; the separation in the amber glass, which may not have been homogeneous itself, was not good because it went to both fractions. The degree of separation should be investigated further for glasses with a density spread of less than 1°.

VII. Limits of Application of Chemical Analysis

Cordy glasses of grade C generally have high color in the polariscope, corresponding to a path difference of 100 or more mμ per cm., or a stress of about 400 lb. per sq. in. The largest stress is developed when the cord is small in cross section compared with the matrix glass, so that it is fully compressed or expanded during cooling to the dimensions demanded by the matrix glass. Using Young's modulus, the expansion difference corresponding to this stress is found to be 10^{-7} per °C., and the available data indicate that composition differences of 0.1% would be necessary to produce this difference in expansion coefficient if, for example, silica were replaced by soda.

From the analyses of the foregoing glasses, it appears that composition differences for cords similar to these would be too small to measure unless density differences are of the order of 2° or 3°C., or 0.004 to 0.006 gm. per cc. Some cordy glasses of grade C with a density spread of less than 1°C. have been separated, and the end fractions were too close in composition to obtain the composition differences. This indicates that, for these small density spreads, the cord either is not completely separated from the matrix glass or the composition differences actually are not large.

TABLE IV

DENSITY SPREAD AS A FUNCTION OF PARTICLE SIZE

Glass No.	Particle size (mesh)	Density spread (°C.)
105	50–100	0.05
	100–150	0.13
	150–200	0.30
	200–325	0.38
65	100–150	7.2
	150–200	8.0
	200–325	12.6
55	150–200	0.33
	200–325	0.51
51	150–200	8.3
	200–325	8.9
49	150–200	2.3
	200–325	2.3
57	150–200	1.2
	200–325	1.2
91	150–200	14
	200–325	23

There would be incomplete separation if the smallest dimension of the cord were much smaller than the particle size used in the powder. Decreasing the particle size would then increase the density spread. Table IV shows that this occurs in some cordy glasses, although it is not generally true. Owing to difficulties connected with the removal of water, whose effect on density becomes greater with smaller particles, no conclusion has yet been reached as to whether the density spread of C cords can generally be increased by taking particles of less than 325-mesh in size. The question as to how widely the method of chemical analysis will be applicable to the study of cords of commercial quality therefore at present remains unanswered. Large composition differences in some of them can be found, and for the others, perhaps another method of attack is necessary.

VIII. Measurement of Physical Properties of Separated Samples

Definite differences in index of refraction of the end fractions are found. The index, however, is roughly proportional to density so that this information gives nothing essentially new. A more important constant is the thermal coefficient of expansion, variations of which are responsible for the low resistance of cordy bottles to thermal shock. A measure of the difference of thermal-expansion coefficient between the end fractions may be found by melting down the samples to a small drop, grinding each surface flat, and melting them together so that they are fused in contact over a plane

surface. This piece may then be ground with two parallel surfaces perpendicular to the contact plane, and, after annealing, it may be examined for stress in a polarizing microscope.

This procedure has been applied to the cordy samples which have been analyzed. The stress has not been measured, but the color observed in the polariscope corresponds to the composition differences indicated in Table II. The cord is in compression in each case so that it has a lower coefficient of expansion than the matrix glass. Measurements of this type might be useful in grading cord, if the cord is completely released and separated from the matrix glass; this latter point should be cleared up first.

Variations in liquidus temperature may be a more sensitive test than chemical analysis for composition differences in the separated fractions, and this is now being investigated.

IX. Summary

Inhomogeneities in bottle glasses can be separated according to density differences if precautions are taken to remove water. Sharp cuts can be made, even on finely ground particles (0.0004 gm. per cc. for 0.002-in. particles). The density spread of inhomogeneous glass, determined by centrifuging, thus affords a direct measure of inhomogeneity.

Density spread is measured in terms of the temperature range over which a separation of the powder can be effected. Bottle glasses of commercial quality show density spreads from scarcely more than 0° to about 3°C., or 0.006 gm. per cc. Noncommercial cordy glasses have been found with density spreads as high as 23°, or 0.05 gm. per cc.

That there is a real separation of glass according to density differences can be shown in several ways. Composition differences of the separated fractions, which are usually measurable for density spreads greater than 2°, or 0.004 gm. per cc., have been found by chemical analysis. For density spreads of 4°, differences of 1% in silica and 0.5% in other major constituents have been found. The separation can also be checked by the measurement of index of refraction, coefficient of thermal expansion, and liquidus temperature.

For all of the inhomogeneities which have been analyzed, the light fractions are relatively high in silica and low in other major constituents. Alumina usually changes very little, but in one case, probably because of a previous batch change, it was high in the light fraction. These cords thus are silica cords caused either by solution of silica refractory or by batch variations or segregation.

No cords had been found (at the time this paper was written) which could be shown to be due directly to solution of aluminous refractory. Since then, however, several cords, accompanied by crystalline material which indicated solution of aluminous refractory as the cause of the cord, have been analyzed and found to be high in alumina. In one of these, alumina increased from 2.9% in the matrix glass to about 7% in the cord.

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MELTING RATE OF SODA-LIME-SILICA GLASSES AS INFLUENCED BY COMPOSITION AND THE EFFECT OF MINOR CONSTITUENTS*

by J. C. Potts

Abstract

Using the disappearance of batch as a criterion of melting, a comparison of the rate of melting of twenty-six soda-lime-silica glass compositions has been made. With the composition, Na_2O 14%, CaO 12%, and SiO_2 (+R_2O_3) 74%, as a base glass, the effect of substituting small amounts of B_2O_3, BaO, SO_3, etc., on the rate of melting was studied. The raw materials used were soda ash, calcite limestone, silica sand, dehydrated borax, barytes, salt cake, Chilean saltpeter, ammonium sulfate, fluorspar, and common salt.

I. Introduction

One phase of a general program which this laboratory began several years ago was the study of the rate of melting of glass as a function of composition. A wide range of compositions in three- and four-component systems were to be investigated, and the data obtained were to be presented in a form easily applicable, at least qualitatively, to plant practice.

The measurement of actual reaction rates is not feasible, and the complexities of the systems are such that the interpretation and application of such data would be extremely difficult. Comparisons of melting rates, however, are easily effected, and they have as much practical value as actual rate measurements. This suggested a suitable method of attack, and two experimental methods for effecting such comparisons have been described.[1] One of these methods proved to be the more convenient, and its use has been continued in the work reported here. The quantity measured is the

* Presented at the Forty-Second Annual Meeting, The American Ceramic Society, Toronto, Canada, April 9, 1940 (Glass Division). Received May 9, 1940.

[1] J. C. Potts, "Comparison of Rates of Melting Glasses Made from Sodium Carbonate, Dolomite Limestone, and Silica Sand," *Jour. Soc. Glass Tech.*, **23** [97] 129–40T (1939); *Ceram. Abs.*, **19** [4] 89 (1940).

time required, at constant temperature, for a small batch to become entirely molten.

The glasses studied fall into three groups as follows: (1) Data are given on twenty-six glasses comprising a portion of the three-component system, Na_2O–CaO–SiO_2, using for raw materials, soda ash, calcite limestone, and silica sand; the range covered was 10 to 18% of Na_2O, 8 to 20% of CaO, and 68 to 80% of SiO_2 (+R_2O_3); (the only R_2O_3 present was introduced as impurities). (2) Explorations were made into the four-component systems (*a*) Na_2O–CaO–B_2O_3–SiO_2 and (*b*) Na_2O–CaO–BaO–SiO_2; dehydrated borax and barytes were used as the sources of B_2O_3 and BaO, respectively. (3) Experiments were performed in which the effect of the introduction of salt cake, saltpeter, common salt, ammonium sulfate, and fluorspar, respectively, into a basic batch was studied. The theoretical composition of all the glasses in this group was approximately the same, that is, 14% of Na_2O, 12% of CaO, 74% of SiO_2 (+R_2O_3).

No glasses were analyzed, and calculated compositions were used throughout.

II. Raw Materials

Commercial grades of raw materials were used except for sodium chloride and ammonium sulfate.

The sand, screened to pass 100-mesh and remain on a 140-mesh U. S. standard sieve, was treated with strong hydrochloric acid to remove as much of the R_2O_3 present as possible, washed well with water, and dried.

The remaining raw materials were screened to pass 100-mesh and remain on 200-mesh U. S. standard sieves. Limestone, barytes, and fluorspar were washed with water to remove adhering fines or dust and were dried at 110°C. All materials except the sand were screened twice.

The following factors were used in calculating the batches:

	SiO_2	R_2O_3	CaO+MgO	Na_2O	B_2O_3	BaO	CaF_2
Sand	99.6	0.17					
Limestone	3.1	0.2	54.2				
Soda ash				58.0			
Dehydrated borax				29.7	66.7		
Barytes	1.75	0.29	0.26			64.0	
Salt cake				43.4			
Chilean saltpeter				36.25			
Fluorspar	2.0	0.05					97.5

III. Experimental Method

Although the method used has been described,[1] it seems desirable to review it briefly.

Weigh enough batch to make 5 grams of glass; mix for 1/2 hour in a small jar mill in which the usual quota of pebbles has been replaced by 3 rubber stoppers and 3 small pebbles. Weigh 1/10 of this batch into a small platinum crucible, place the crucible and charge in a platinum wire basket, and raise the ensemble quickly into place in the furnace (Fig. 1). After an arbitrary period of time, lower the melt from the furnace (it will chill rapidly and in less than 1 minute will be cool enough to handle). Examine the melt under a low-power microscope (50×). If the melt is batch-free, repeat the experiment using a shorter time; if batch is still present, use a longer time in the next test.

This method thus is essentially one of trial and error, and a number of melts must be made for each composition studied.

All melts were made at 1427° ± 3°C. (2600°F.).

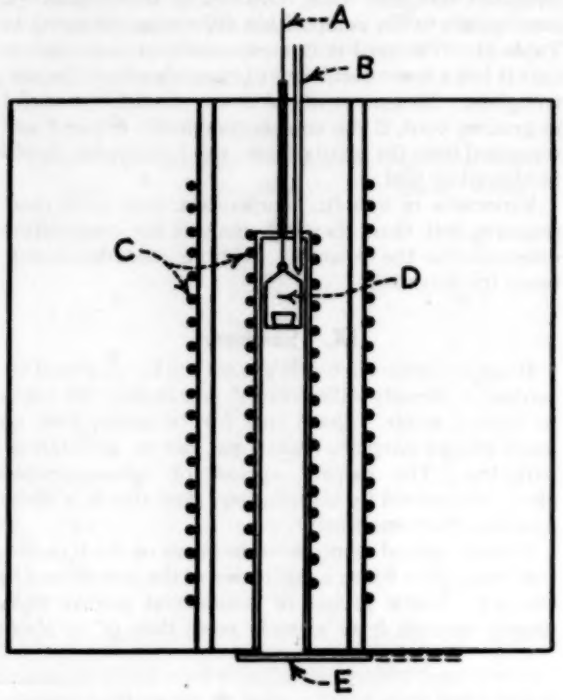

FIG. 1.—*A*, platinum suspension wire for cage; *B*, thermocouple; *C*, platinum furnace windings; *D*, wire cage containing crucible and charge; *E*, sliding furnace cover plate.

IV. Experimental Results

The actual experimental data are shown only graphically, and all of the tabulated values are readings from the various smooth curves.

Figure 2 shows the data for one of the seven series of melts which comprise that portion of the three-component system, Na_2O–CaO–SiO_2, studied. The ordinate scale, representing time in minutes, is logarithmic and was chosen for convenience in plotting. The circles (*a*) represent melts which appear to be definitely free of batch; the crosses (*b*) melts which were unquestionably incompletely molten; the triangles (*c*) those melts which fell into neither of the (*a*) and (*b*) classes. In these melts, a small cluster of grains more often than not suggests

that a slight amount of segregation has taken place. A smooth curve drawn through these points gives a good estimate of the melting time for each glass.

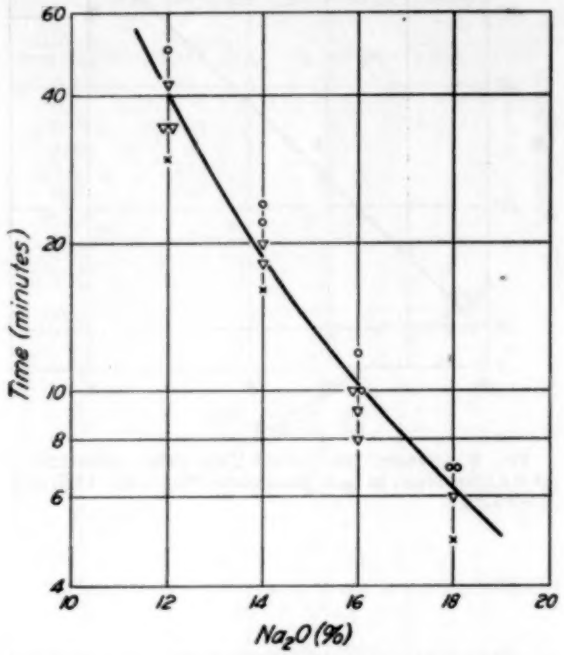

FIG. 2.—System Na_2O–CaO–SiO_2; effect of substituting Na_2O for SiO_2 (CaO 10%).

Smooth-curve values† taken from Fig. 2, together with those from similar figures (not shown) for the six remaining series, are given in Table I. Using these data as a basis, Fig. 3 has been constructed, which shows contours of constant melting time at 1427°C.

Figures 4 to 7, inclusive, show the effect of substituting B_2O_3 for Na_2O, CaO, SiO_2, and (Na_2O + SiO_2), respectively, in the base glass, Na_2O 14%, CaO 12%, and SiO_2 74%; solid circles indicate values from Table I; the smooth-curve values are given in Table II.

Figures 8 to 11, inclusive, show data for melts containing barytes. Figure 8 shows the effect of substituting small amounts of BaO for SiO_2 in four base glasses, containing 14% of Na_2O and 8%, 10%, 12%, and 14% of CaO, respectively. Figure 9 shows the effect of substituting BaO for Na_2O and CaO, respectively, in the base glass with 14% of Na_2O and 12% of CaO (note that 8(*C*) shows the effect of BaO for SiO_2 in this base glass). Figures 10 and 11 show the effect of substituting CaO for SiO_2 in glasses containing 14% of Na_2O

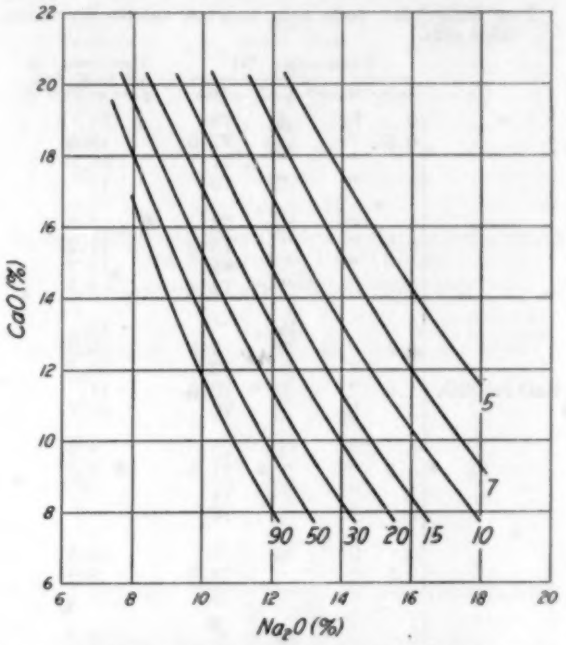

FIG. 3.—System Na_2O–CaO–SiO_2; lines of constant melting time at 1427°C. (time in minutes).

TABLE I

SYSTEM Na_2O–CaO–SiO_2

Raw materials: sodium carbonate, raw calcite limestone, and silica sand

Time (min.) to obtain batch-free glass at 2600°F.

CaO (%)	Na_2O (%) 8	10	12	14	16	18
8			90	34	16.5	9.6
10			44	19.5	10.6	
12		100	30	13	7.2	
14		48	18.7	9.5	5.5	
16	120	29	12.3	6.7	4.3	
18	50	18	8.8			
20	24	10.5	5.7			

† Some smooth-curve values are given to one place more than the accuracy of the data warrants in order to bring the various curves into agreement.

TABLE II

SYSTEM Na_2O–CaO–B_2O_3–SiO_2

Raw materials: soda ash, calcite limestone, dehydrated borax, silica sand

	Composition (%) B_2O_3	Na_2O	CaO	SiO_2	Time (min.) to obtain batch-free glass at 2600°F.
B_2O_3 for Na_2O	0	14	12	74	13
	0.25	13.75	"	"	11
	0.50	13.50	"	"	12
	1	13	"	"	15
	3	11	"	"	36
	5	9	"	"	88
B_2O_3 for CaO	0	14	"	"	13
	0.5	"	11.5	"	11.5
	1	"	11	"	12.5
	3	"	9	"	20
	5	"	7	"	31
B_2O_3 for SiO_2	0	"	12	"	13
	0.5	"	"	73.5	10.5
	1	"	"	73	"
	3	"	"	71	"
	5	"	"	69	"
B_2O_3 for Na_2O + SiO_2	0	"	"	74	13
	0.5	13.75	"	73.75	12
	1	13.50	"	73.50	14
	3	12.50	"	"	24
	5	11.50	"	71.5	43

and 1/4% of BaO, and 14% of Na_2O and 1% of BaO, respectively. The dotted curves represent glasses of corresponding Na_2O and CaO content but containing no BaO. The smooth-curve data for all BaO glasses are given in Table III (see + footnote, p. 45).

TABLE III

SYSTEM Na_2O–BaO–CaO–SiO_2

Raw materials: soda ash, barytes, calcite limestone, silica sand

	Composition (%)				Time (min.) to get batch-free glass at 2600°F.
	BaO	Na_2O	CaO	SiO_2	
BaO for SiO_2	0	14	8	78	34
	0.5	"	"	77.5	19.5
	1	"	"	77	16.5
	2	"	"	76	11
	0	"	10	76	19.5
	0.5	"	"	75.5	11.2
	1	"	"	75	12.2
	2	"	"	74	9.5
	0	"	12	"	13
	0.5	"	"	73.5	8.2
	1	"	"	73	10.7
	1.5	"	"	72.5	11
	2	"	"	72	10.7
	0	"	14	72	9.5
	0.5	"	"	71.5	8.2
	1	"	"	71	"
	2	"	"	70	"
	0	16	8	76	16.5
	0.5	"	"	75.5	8.2
	1	"	"	75	11.5
	0	"	10	74	10.6
	0.5	"	"	73.5	5.7
	1	"	"	73	8.9
BaO for Na_2O	0	14	12	74	13
	0.5	14.5	"	"	8.2
	1	13	"	"	12.2
	1.5	12.5	"	"	12.4
	2	12	"	"	12.6
BaO for CaO	0	14	12	"	13
	0.5	"	11.5	"	8
	1	"	11	"	11.2
	1.5	"	10.5	"	11.6
	2	"	10	"	9.5

The five remaining figures (Figs. 12 to 16, inclusive) show the effect of introducing $(NH_4)_2SO_4$, Na_2SO_4, $NaNO_3$, NaCl, and CaF_2 into the base glass, Na_2O 14%, CaO 12%, and SiO_2 74%. The smooth-curve values for these melts are given in Tables IV to VIII, inclusive.

TABLE IV

EFFECT OF ADDING AMMONIUM SULFATE TO BASE GLASS

(Na_2O 14%, CaO 12%, and SiO_2 74%)

$(NH_4)_2SO_4$ (lb.)/ T. of glass	SO_3 (lb.)/ T. of glass	Time (min.) to obtain batch-free glass at 2600°F.
0	0	13.0
8.6	5.2	8.5
17.2	10.5	13.5
51.6	31.2	12.0

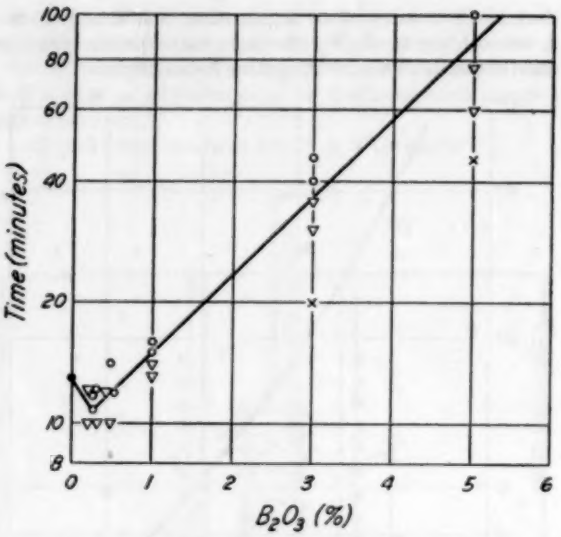

FIG. 4.—System Na_2O–CaO–B_2O_3–SiO_2; substitution of B_2O_3 for Na_2O in base glass containing Na_2O 14% and CaO 12%.

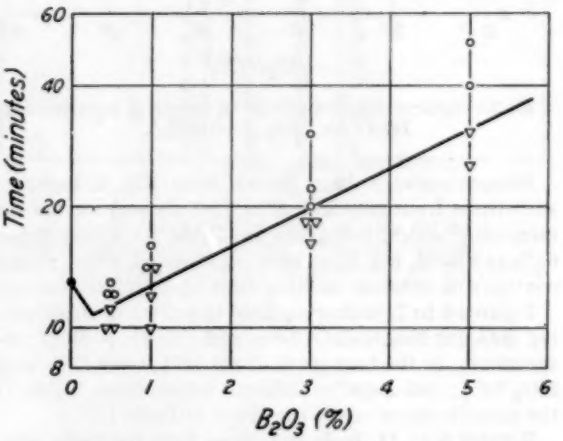

FIG. 5.—System Na_2O–CaO–B_2O_3–SiO_2; substitution of B_2O_3 for CaO in base glass containing Na_2O 14% and CaO 12%.

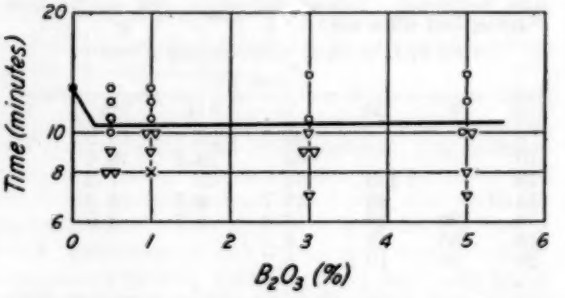

FIG. 6.—System Na_2O–CaO–B_2O_3–SiO_2; substitution of B_2O_3 for SiO_2 in base glass containing Na_2O 14% and CaO 12%.

TABLE V

EFFECT OF PARTIAL SUBSTITUTION OF SALT CAKE FOR SODA ASH IN BASE GLASS

(Na_2O 14%, CaO 12%, and SiO_2 74%)

Na_2O (%) from Na_2SO_4	Na_2SO_4 (lb.)/T. glass	SO_3 (lb.)/T. glass	Time (min.) to obtain batch-free glass at 2600°F.
0.0			13.0
0.2	9.2	5.2	7.5
0.5	23.3	13.1	11.5
1.0	46.5	26.2	13.5
3.0	140.0	79.0	10.5
5.0	233.0	131.0	13.0

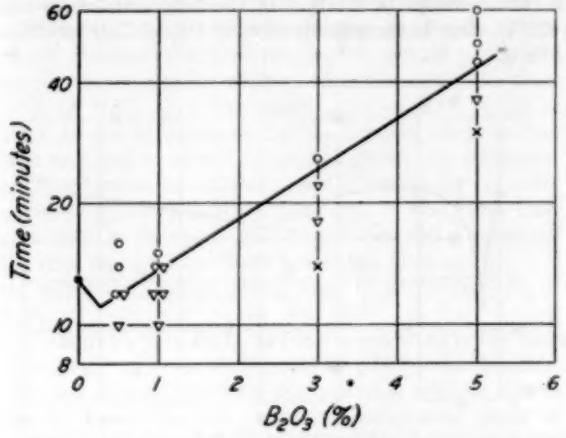

FIG. 7.—System Na_2O–CaO–B_2O_3–SiO_2; substitution of $2B_2O_3$ for Na_2O + SiO_2 in base glass containing Na_2O 14% and CaO 12%.

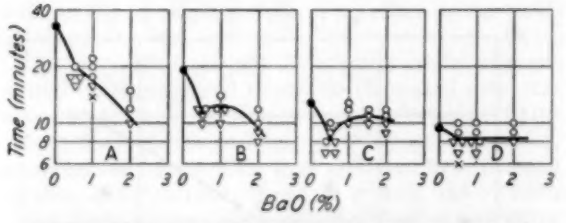

FIG. 8.—System Na_2O–BaO–CaO–SiO_2; substitution of BaO for SiO_2 in four different base glasses; base glasses are (*A*) Na_2O 14%, CaO 8%; (*B*) Na_2O 14%, CaO 10%; (*C*) Na_2O 14%, CaO 12%; (*D*) Na_2O 14%, CaO 14%.

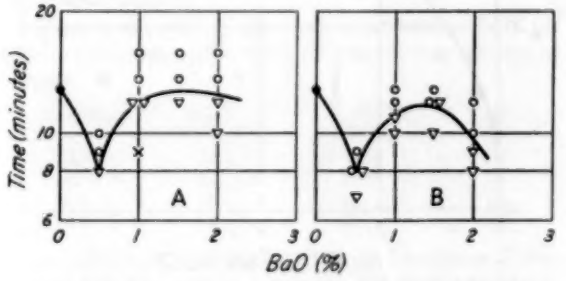

FIG. 9.—System Na_2O–BaO–CaO–SiO_2; (*A*) BaO for Na_2O; (*B*) BaO for CaO; base glass contains Na_2O 14% and CaO 12%.

V. Discussion

In spite of a definitely quantitative appearance, these data must be regarded as essentially qualitative,

TABLE VI

EFFECT OF PARTIAL SUBSTITUTION OF COMMON SALT FOR SODA ASH IN BASE GLASS

(Na_2O 14%, CaO 12%, and SiO_2 74%)

Na_2O (%) from NaCl	NaCl (lb.)/T. glass	Time (min.) to obtain batch-free glass at 2600°F.
0	0	13
0.5	18.9	21
1	37.8	28
2	75	40
3	113	54

TABLE VII

EFFECT OF PARTIAL SUBSTITUTION OF CHILEAN SALTPETER FOR SODA ASH IN BASE GLASS

(Na_2O 14%, CaO 12%, and SiO_2 74%)

Na_2O (%) from $NaNO_3$	$NaNO_3$ (lb.)/T. glass	Time (min.) to obtain batch-free glass at 2600°F.
0	0	13
0.5	27.4	21
1	54.8	30
2	110	37
3	164	30
4	219	28
5	274	45

TABLE VIII

EFFECT OF SUBSTITUTING FLUORSPAR FOR CALCITE LIMESTONE IN BASE GLASS

(Na_2O 14%, CaO 12%, and SiO_2 74%)

CaO (%) from CaF_2	CaF_2 (lb.) /T. glass	F (%) /T. glass	Time (min.) to obtain batch-free glass at 2600°F.
0	0	0	13
0.38	10.6	0.25	13
0.76	21.1	0.5	13.5
1.52	42.2	1.0	13.5
3.03	84.4	2.0	13.5

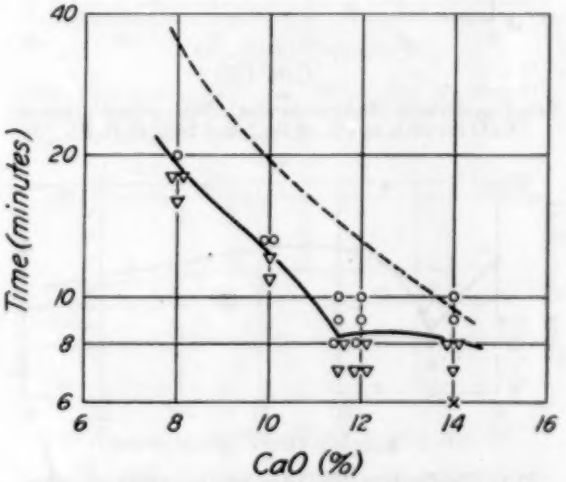

FIG. 10.—System Na_2O–BaO–CaO–SiO_2; substitution of CaO for SiO_2 at $^1/_2$% of BaO and 14% of Na_2O.

because a number of factors are involved in these experiments which either cannot be accurately measured or cannot be adequately controlled. To place these data on a quantitative basis, for example, it would be necessary to apply a correction for the amount of reaction which does not take place during the initial period (90 to 100 seconds) while the batch is heating up. A second example is the virtual impossibility of preparing, on different occasions, two or more lots of the same batch material in which the distribution of grain shapes and grain sizes would be identical.

Undue stress should not be laid on the inability to control such factors, for, in large-scale operations, other variables, such as temperature gradients and convection currents, come into play and render the application of these data qualitative in any event.

The experimental errors involved in this work are not easily estimated. The base glass, Na_2O 14%, CaO 12%, and SiO_2 74%, has been run on several widely separated occasions, and the data have agreed excellently. The compositions are such that the experimental points in a number of cases may be plotted several ways. The best smooth curves drawn in these various plots yield substantially the same melting times for the individual glasses. This, of course, indicates only that the data are self-consistent.

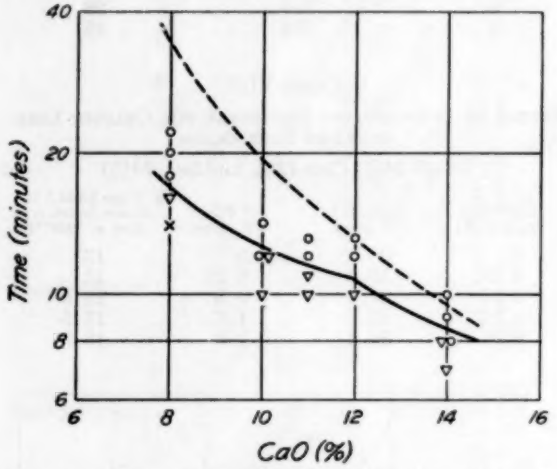

FIG. 11.—System Na_2O–BaO–CaO–SiO_2; substitution of CaO for SiO_2 at 1% of BaO and 14% of Na_2O.

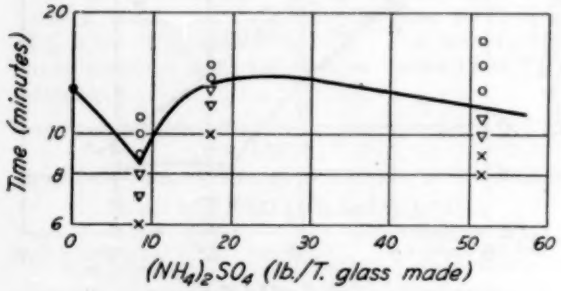

FIG. 12.—System Na_2O–CaO–SiO_2; effect of introducing ammonium sulfate into batch; base glass: Na_2O 14%, CaO 12%, and SiO_2 74%.

(1) Soda-Lime-Silica Glasses

Examination of Fig. 3 or of the data in Table I enables the following conclusions to be drawn: (*a*) Substitution of Na_2O (as 100- to 200-mesh soda ash) for SiO_2 (100- to 140-mesh sand) materially decreases the time required to obtain complete solution of batch materials at 1427°C.; (*b*) substitution of CaO (100- to 200-mesh calcite limestone) for SiO_2 materially decreases the time required to obtain complete solution of the batch materials at 1427°C.; and (*c*) within the range of compositions studied, the substitution of 1% of Na_2O for 1% of SiO_2 is more effective in decreasing the time required to obtain complete solution of the batch materials at 1427°C. than is the substitution of 1% of CaO for 1% of SiO_2.

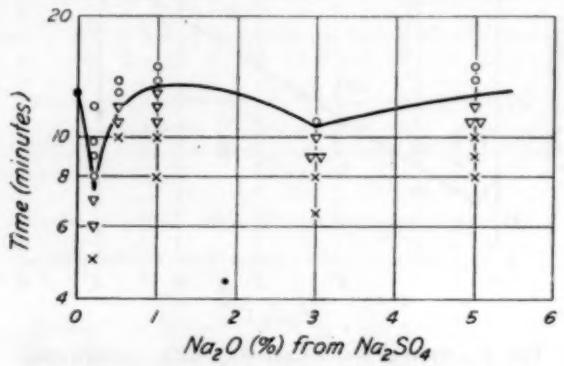

FIG. 13.—System Na_2O–CaO–SiO_2; effect of substituting salt cake for part of soda ash; base glass: Na_2O 14%, CaO 12%, and SiO_2 74%.

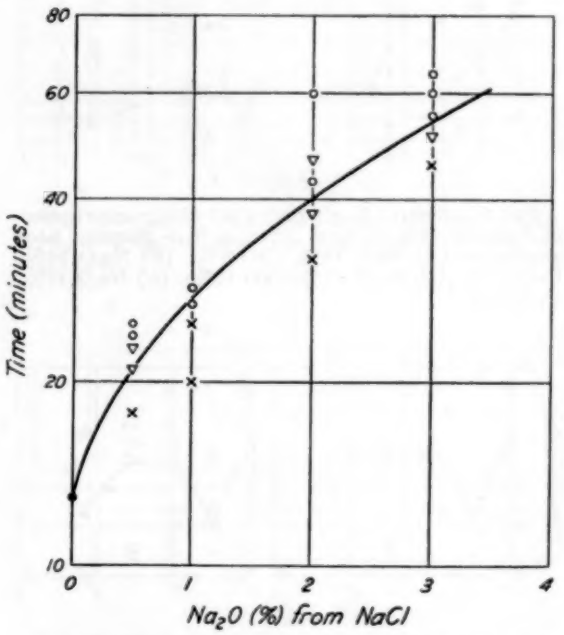

FIG. 14.—System Na_2O–CaO–SiO_2; effect of substituting common salt for part of soda ash; base glass: Na_2O 14%, CaO 12%, and SiO_2 74%.

(2) Borax Glasses

The best representation of the experimental data seems to be given by a broken line (as shown in Figs. 4 to 7) rather than by a smooth curve; it also seems reasonable to draw all four minima at about the same B_2O_3 content, namely, 1/4%.

For substitutions in the base glass, Na_2O 14%, CaO 12%, and SiO_2 74%, the following conclusions may be drawn: (*a*) The substitution of B_2O_3 (as 100- to 200-mesh dehydrated borax) for Na_2O first slightly decreases and then appreciably increases the time required to obtain batch-free glass at 1427°C.; the minimum time is at 1/4% (or less) of B_2O_3. (*b*) The substitution of B_2O_3 for CaO first slightly decreases and then appreciably increases the time required to obtain batch-free glass; the minimum melting time occurs at less than 1/2% of B_2O_3. (*c*) The substitution of B_2O_3 for SiO_2, after an initial decrease, has no further effect on the time required to obtain batch-free glass; the minimum melting time occurs at less than 1/2% of B_2O_3. (*d*) The substitution of B_2O_3 for equal parts of Na_2O and SiO_2 first slightly decreases and then appreciably increases the time required to obtain batch-free glass at 1427°C.; the minimum melting time occurs at less than 1/2% of B_2O_3.

If about 1/4% of B_2O_3 has been substituted in the base glass, Na_2O 14%, CaO 12%, and SiO_2 74%, a further substitution of B_2O_3 produces the following relative effects on the time required to obtain batch-free glass at 1427°C.: (i) 2% of B_2O_3 for 2% of Na_2O increases the melting time appreciably; (ii) 2% of B_2O_3 for 1% of Na_2O plus 1% of SiO_2 increases the melting time less than (i); (iii) 2% of B_2O_3 for 2% of CaO increases the melting time slightly less than (ii); and (iv) 2% of B_2O_3 for 2% of SiO_2 has little or no effect on the melting time.

The surface of the 5% B_2O_3 melts containing unmelted batch appeared cloudy to the naked eye. On examination with the low-powered microscope, however, a fine network of lines, probably surface cracks, was observed; some of the lines appeared to be in small patches, and sometimes the entire surface was covered. These "crizzled" patches were not present in batch-free melts.

In calculating the batches for the B_2O_3 glasses, allowance was made for the Na_2O contributed by the dehydrated borax.

(3) BaO Glasses

Figure 8 shows the effect of substituting BaO (as 100- to 200-mesh barytes) for SiO_2 in the four glasses as follows:

Glass No.	Na_2O (%)	CaO (%)	SiO_2 (%)
A	14	8	78
B	14	10	76
C	14	12	74
D	14	14	72

The substitution of BaO for SiO_2 in base glass *C* produces a definite minimum in the time required to obtain batch-free glass at 1427°C.; this minimum is near the composition Na_2O 14%, CaO 12%, BaO 1/2%, and SiO_2 73 1/2%. Similar substitutions in base glasses *A*, *B*, and *D* indicate a minimum melting time or at least a break in the curve at some BaO content of less than 1%.

The observations are summarized in (*a*) and (*b*) as follows:

(*a*) The substitution of less than 2% of BaO (as 100- to 200-mesh barytes) for SiO_2 in glasses containing 14% of Na_2O and from 8% to 14% of CaO decreases the time required to obtain batch-free glass at 1427°C.; the amount of the decrease is variable and does not vary regularly with either the CaO or BaO content. Figure 9 shows the effect of substituting BaO for Na_2O (9*A*), and BaO for CaO (9*B*) in base glass *C*, Na_2O 14%, CaO 12%, and SiO_2 74%. The curves are similar to 8(*C*).

(*b*) Therefore the substitution of BaO in amounts of less than 2% for Na_2O, CaO, or SiO_2 in the base glass, Na_2O 14%, CaO 12%, and SiO_2 74%, has approximately the same effect on the time required to obtain batch-free glass at 1427°C. whether the substitution be BaO for Na_2O, BaO for CaO, or BaO for SiO_2. A minimum melting time is observed in each case for the glass containing approximately 1/2% of BaO.

Figures 10 and 11 are "cross-plots" of the data given in Fig. 8 and show the effect of the substitution of CaO for SiO_2 at 14% of Na_2O and 1/2% of BaO and at 14% of Na_2O and 1% of BaO. The dotted curves represent

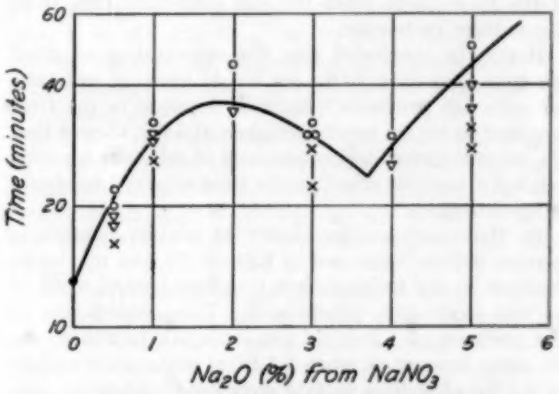

FIG. 15.—System Na_2O–CaO–SiO_2; effect of substituting Chilean saltpeter for part of soda ash; base glass: Na_2O 14%, CaO 12%, and SiO_2 74%.

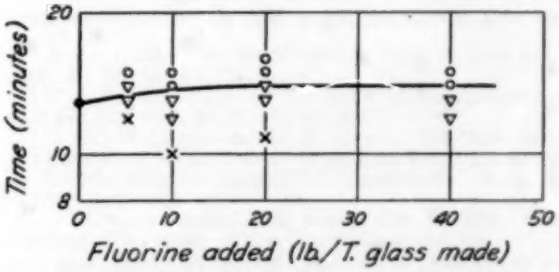

FIG. 16.—System Na_2O–CaO–SiO_2; effect of substituting fluorspar for part of limestone; base glass: Na_2O 14%, CaO 12%, and SiO_2 74%.

data from Table I for the same substitution at 14% of Na_2O and no BaO.

(4) Refining Agents

When the batches for this group of glasses were calculated, it was assumed that all of the gaseous products, that is, NH_3, CO_2, SO_3, Cl_2, F_2, and NO_2, would be completely volatilized; and, as allowance was made for the Na_2O or CaO available in the refining agent, all of the resultant glasses have the same theoretical composition. In practice, of course, this result was not attained, and the twenty-one glasses discussed here have slightly different compositions.

Figure 12 shows the effect of adding ammonium sulfate to the batch. A minimum is again observed, this time when 8.6 lb. of ammonium sulfate per ton of glass made had been added.

The conclusion may be drawn that the addition of small amounts (less than 15 lb. per ton of glass made) of ammonium sulfate to the batch produces a decrease in the time required to obtain batch-free glass at 1427°C. The addition of larger amounts of ammonium sulfate produces a variable effect on the time required to obtain batch-free glass.

Figure 13 shows the effect of replacing part of the soda ash by salt cake. In this substitution, a sharp minimum appeared when 0.2% of Na_2O was derived from the salt cake and 13.8% from the sodium carbonate. There was also a slight minimum when 3% of the Na_2O came from the salt cake and 11% from the sodium carbonate.

It may be concluded that the substitution of small amounts (less than 70 lb. per ton of glass) of salt cake for soda ash produces a definite decrease in the time required to obtain batch-free glass at 1427°C. and that the substitution of larger amounts of salt cake for soda ash has a variable effect on the time required to obtain batch-free glass.

In the corresponding series of glasses containing barium sulfate, discussed in section (3), the maximum decrease in the melting time was found when 0.5% of barium oxide was substituted. This corresponds to the presence of 5.2 lb. of available SO_3 in the batch, the same amount as when 8.6 lb. of ammonium sulfate or 9.2 lb. of sodium sulfate were used. It seems possible that the presence of these minima in the melting times of these three series of glasses is due to the presence of sulfate, but this may be accidental.

Figure 14 shows the effect of a partial substitution of sodium chloride for sodium carbonate. It is evident that the substitution of common salt for soda ash markedly increases the time required to obtain batch-free glass at 1427°C.

Figure 15 shows the effect of a similar substitution in which sodium nitrate replaces sodium carbonate. This figure also shows that the substitution of Chilean saltpeter for soda ash markedly increases the time required to obtain batch-free glass at 1427°C. The data indicate a minimum melting time in the neighborhood of the composition where $3^1/_2$% of the Na_2O comes from the saltpeter and $10^1/_2$% from the sodium carbonate.

Figure 16 shows the effect of introducing fluorine as calcium fluoride into the batch of the base glass. In this series of glasses, calcium from fluorspar was substituted for calcium from calcite limestone. The substitution of fluorspar for calcite limestone (with the accompanying introduction of fluoride) therefore has a negligible effect on the time required to obtain batch-free glass at 1427°C.

VI. Summary

Data have been presented which enable comparisons to be made of the melting rates of seventy-one glass batches.

Although it is possible in systems which show marked regularities (e.g., soda ash–limestone–sand) to make predictions about the melting rates of compositions not actually studied, it is not true in general because the magnitude as well as the direction of the effect of a given substitution will vary with the initial batch. This, plus the fact that frequently insufficient attention is given to such factors as grain size (or screen analysis) and temperature, may account for some of the conflicting reports to be found in the glass literature.

Acknowledgment

The author wishes to acknowledge the assistance of V. C. Rees in performing a number of the experiments reported here.

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ELECTROLYTES IN ACID-RESISTING ENAMELS*

By Fred A. Petersen and Clark Hutchison

Abstract

The effect of various electrolytes on the acid resistance, "set," and defects of acid-resisting enamels was studied. The defects encountered were scumming, pitting, and shorelining. It was found that (1) insufficient set caused scumming which was aggravated by aging the enamel; this defect may be eliminated by increasing the set of the enamel; (2) one of the enamels studied had a marked tendency to shoreline whenever a sulfate or an electrolyte containing the sulfate radical was used; and (3) the pitting tendency of one enamel was traced to the high soluble salt content of the mill liquor; this defect was eliminated by spraying the enamel at a high gravity or by applying the acid-resisting enamel in a heavier coating. Some of this work has been continued in regular plant practice, and a discussion of this phase of the work is included.

I. Introduction

"Set" is the name given to one of the factors that has a decided effect on the workability of acid-resisting enamels. Improper set causes difficulty in handling the enamel and contributes to several defects which are characteristic of acid-resisting enamels.

In this investigation, the effect of various electrolytes on the set, acid resistance, and defects produced in stainless enamels was studied.

(1) Review of the Literature

Harrison[1] discusses the mechanism of enamel suspension, and he lists data collected in plant tests by the use of a consistometer designed for plant control. His conclusions are given under four headings, viz., (1) constitution of enamel slips, (2) fundamental factors concerning consistency, (3) measurement of properties governing consistency, and (4) obtaining slips of desired consistency.

Several investigators have studied the soluble salts which are found in enamel slips. Whitesell[2] found that aging the enamel at high temperatures increased considerably the amount of soluble salts which acted as fluxes and decreased underfire scum. He also states that tearing increased with an increase of soluble salts.

Danielson[3] found that when some enamels are dried slowly crystals of borax and other soluble salts are formed which show up in the firing as pits. Lowering the borax content eliminates this defect. A plant check showed that a white enamel does not begin to crystallize and pit until the soluble salts are about twice the quantity which caused these same defects under laboratory conditions. He also states that solution of the frit is dependent on the composition of the glass. Enamels, which are excessively alkaline, owing to the solution of a considerable amount of free alkali from the glass, have poor floating properties and those with excess borax in the mill liquor tend to pit and crawl.

Cooke[4] concludes that in order to obtain "setting up" in an enamel there must be more than one salt present. Only the mineral acids "set-up" the enamel when no other salts are present, but the action is caused by the formation of a bulky insoluble compound in the presence of several salts.

Cook[5] states that the solution of the enamel frit increases as fineness increases. Variations in smelting and mixing of the raw materials have little effect on the solubility.

On dry grinding, Na_2O and B_2O_3 immediately dissolve from the frit when it is treated with water. Chemical analysis of the mill liquor shows that it contains siliceous material, alumina, and sodium salts of carbonate, sulfate, chloride, and borate; the sodium borate is present in the greatest amount.

McIntyre and Bevis[6] conclude that there is a definite relationship between soluble salts and enamel consistency but that other factors should be considered. They also report[7] on the effect of the ratio of soda to boric oxide on such properties of the enamel slip as pH, yield value, and mobility.

Cook[8] studied the setting-up action of various electrolytes on a clay slip, a milled enamel, a suspension of clay and silica sand in water, and on silica sand and water. He concludes that (1) the setting up of water suspensions of finely divided insoluble materials does not seem to depend on the presence of clay; (2) it is impossible to get the stiffening action with an electrolyte in a clay slip that is obtained in an enamel slip with the same water content; (3) fineness of grinding and degree of solution of the suspended material are more important factors than the

* Presented at the Forty-Second Annual Meeting, The American Ceramic Society, Toronto, Canada, April 10, 1940 (Enamel Division). Received April 23, 1940.

[1] W. N. Harrison, "Controlling Consistency of Enamel Slips," *Jour. Amer. Ceram. Soc.*, **10** [12] 970–94 (1927); *Bur. Stand. Tech. Paper*, No. 356, 34 pp. (1927).

[2] R. J. Whitesell, "Effect of Soluble Salts Formed During Aging on Scumming of Enamels," *Jour. Amer. Ceram. Soc.*, **20** [3] 72–75 (1937).

[3] R. R. Danielson, "Effect of Soluble Salts on Properties of Enamels," *ibid.*, **12** [8] 538–47 (1929).

[4] R. D. Cooke, "Study of Soluble Salts in Enamels," *ibid.*, **13** [9] 658–61 (1930).

[5] H. L. Cook, "Note on Solubility of Enamel Frit in Mill Water," *ibid.*, **10** [5] 339–43 (1927).

[6] G. H. McIntyre and R. E. Bevis, "Frit Solubility: I, Comparison of Methods of Determination and Relation of Soluble Salts to Enamel-Slip Consistency," *ibid.*, **19** [9] 249–52 (1936).

[7] G. H. McIntyre and R. E. Bevis, "Frit Solubility: II, Controlled Variables of Frit Composition and Their Relation to Enamel Consistency," *ibid.*, **21** [5] 184–88 (1938).

[8] H. L. Cook, "Observations on Effect of Various Electrolytes When Added to Enamel Suspensions With and Without Clay," *ibid.*, **10** [5] 344–46 (1927).

floating power of the clay used; (4) electrolytic charging on the colloidal particles possibly comes into play in the phenomena studied; and (5) clayless suspensions are not advocated because the use of clay in an enamel results in a piece that is easier to handle after it is dried.

Several investigators[9] have reported that acid-resisting enamels have various shortcomings, such as lack of opacity, difficulty of suspension, tendency to hairline, tendency to blister owing to the high viscosity at the fusion temperature, sagging, "poppers," and shorelines. The specific gravity of acid-resisting enamels does not affect the acid resistance, but it will affect the surface defects.

Various electrolytes have been listed[10] as suitable for setting up enamels. Some of the more common of these are magnesium, ammonium, and potassium carbonates; alum; calcium, barium, and ammonium chlorides; Epsom salts; sodium aluminate; and the mineral acids. Raw zinc oxide, precipitated barium carbonate, and light magnesium carbonate in the presence of soluble boric acid in the mill batch of raw glazes cause a stiffening action of the glazes on standing.

Chlorides and sulfates are said by Otremba[11] to cause a dulling of the enamel.

Shorelines are attributed by Hansen[12] and Knowles[13] to be the result of the deposition of soluble salts during the drying process. The condition is aggravated by fast drying and drying with a low humidity. This defect is characteristic of acid-resisting enamels.

Redd[14] cites, as a cause for shorelines, the milling of acid-resisting enamels at too high a temperature, which increases the soluble salts.

II. Procedure

Two stainless frits were used as the basis for this investigation. To determine any characteristic differences in the frits, extractions were made using the standard Soxhlet apparatus, and the extracts were analyzed for Na_2O, B_2O_3, and total solids.

The mill liquors of the two base enamels, milled without any electrolytes present, were also analyzed for Na_2O and B_2O_3.

The enamel frit was milled, using the following mill batch: frit 100, clay 5, opacifier 5, electrolyte 4 oz. (variable, see Table I), and water 40.

Enamels were milled in 1-gallon laboratory mills to a fineness of 3 to 5 gm. residue from a 100-gm. sample of slip, and they were set at a specific gravity of 1.80. Consistency was checked with a two-tube consistometer. Observations were also made on the workability of the enamel and on the condition of the enamel before use. The enamels were applied at 25 to 28 gm. per sq. ft. to duplicate 6- by 12-inch panels which had previously been given a ground coat and one coat of superopaque cover enamel (25 to 28 gm. per sq. ft.). All of the plates were dried and fired for 3 minutes in an electric laboratory furnace at 1500°F. A "spot" test was employed to determine the relative acid resistance of the fired enamels, and the plates were carefully inspected for surface defects. The enamels were then aged for seven days, and the test was repeated.

The next step was the determination of the effect of adding the electrolytes to the milled enamel. Mills of the two base frits of 25 lb. each, containing no electrolytes, were milled to a fineness of 3 to 5 gm. and were set at a specific gravity of 1.80. Only the easily soluble electrolytes were used in this part of the investigation because the slightly soluble salts could not be added to the milled enamel so as to give a uniform distribution throughout the enamel. The electrolytes were dissolved in water and added to separate portions of the milled enamel, and the procedure outlined for the first part of the investigation was repeated.

From the results obtained in these tests, several electrolytes were selected and added in various amounts and combinations, and certain defects encountered in plant practice were eliminated by this procedure.

III. Testing Methods

The fineness of the enamels was determined by the Porcelain Enamel Institute tentative standard test for fineness of wet-milled enamels.[15]

Acid resistance was determined by a "spot" test. Several drops of 10% citric acid were placed on the enameled surface and allowed to remain for 15 minutes; the plate was then cleaned with water and dried, and the acid resistance was rated by visual inspection.

Consistency determinations were made by using a two-tube consistometer.[16]

Frit extractions were made with the regular Soxhlet apparatus. A 60-gm. sample of frit, screened through a 30-mesh sieve and retained on an 80-mesh sieve, was extracted for 8 hours, using 100 ml. of distilled water.

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[9] (*a*) W. N. Noble, "Application of Sheet-Iron Acid-Resisting Enamel," *Enamelist*, **13** [3] 8–9 (1935); *Ceram. Abs.*, **15** [3] 83 (1936).
(*b*) G. H. Spencer-Strong, "Factors Influencing Properties of Acid-Resisting Enamels," *Jour. Amer. Ceram. Soc.*, **21** [1] 1–8 (1938).
(*c*) D. B. Walters, "Progress in Field of Acid-Resisting Enamels," *Better Enameling*, **5** [3] 8–9 (1934); *Can. Chem. Met.*, **18** [3] 53 (1934); *Ceram. Abs.*, **13** [6] 142 (1934).

[10] (*a*) J. E. Hansen (editor), Manual of Porcelain Enameling, pp. 123–25. Enamelist Publishing Co., Cleveland, Ohio, 1937; *Ceram. Abs.*, **17** [2] 59 (1938).
(*b*) W. K. Carter, "Sodium Aluminate for Setting Up Enamel Slips," *Ceram. Ind.*, **21** [4] 184–85 (1933); *Ceram. Abs.*, **12** [12] 414 (1933).
(*c*) K. M. Kautz, "Effect of Boric Acid in Raw Milled Glazes," *Jour. Amer. Ceram. Soc.*, **15** [11] 638–43 (1932).
(*d*) J. T. Irwin, "Acid Resistance and Production Problems," *Enamelist*, **15** [7] 10–12 (April, 1938).
(*e*) Franz Novak, "Setting Enamels with Hydrochloric Acid," *Amer. Enameler*, **8** [2] 4 (1935); *Ceram. Abs.*, **14** [11] 271 (1935).
(*f*) "Electrolytes in Enamel Industry," *Glashütte*, **64** [6] 85–87 (1934); *Ceram. Abs.*, **13** [10] 250 (1934).

[11] A. Otremba, "Influence of Electrolytes on Enamels," *Keram. Rundschau*, **34**, 506–507 (1926); *Ceram. Abs.*, **5** [11] 343 (1926).

[12] Hansen, *op. cit.*, pp. 193 and 317.

[13] W. V. Knowles, "Shorelines," *Better Enameling*, **8** [4] 32 (1937).

[14] O. F. Redd, "Milling Porcelain Enamel Under Controlled Thermal Conditions," *Enamelist*, **14** [10] 14–15 (1937); *Ceram. Abs.*, **16** [11] 330 (1937).

[15] "Tentative Screen Test for Wet-Milled Porcelain Enamel." Porcelain Enamel Institute, November, 1938.

[16] J. T. Irwin and R. E. Bevis, "Modification of the Bingham Plastometer," *Jour. Amer. Ceram. Soc.*, **21** [2] 66–68 (1938).

The extracted solution was titrated for Na_2O and B_2O_3, and the total solids were determined.

The mill liquors of the two base frits were titrated to determine their Na_2O and B_2O_3 content.

The sample was titrated with standard acid to the methyl orange end point for the Na_2O determination. Mannitol was added, and the B_2O_3 was titrated with standard base to the phenolphthalein end point.

are listed in Table II. Table III gives the soluble salts found in the extractions of the enamel frits.

Data concerning defects encountered in using the various electrolytes studied and the relative set of the enamels are given in Tables IV and V.

The set ratings were calculated from a combination of the results obtained in the consistency studies and data gathered by observing the condition of the enamel

TABLE I

Electrolyte	Chemical formula	Solubility (gm./100 ml. of water)* Cold	Hot
Carbonates			
Magnesium (light)	$3MgCO_3 \cdot Mg(OH)_2$	0.04	0.011
Ammonium	$(NH_4)_2CO_3 \cdot H_2O$	100	d.
Potassium	K_2CO_3	112	156
Calcium	$CaCO_3$	0.0014	0.0018
Sodium	Na_2CO_3	7.1	45.5
Barium	$BaCO_3$	0.002	0.006
Sulfates			
Magnesium (Epsom salts)	$MgSO_4 \cdot 7H_2O$	71	91
Ammonium	$(NH_4)_2SO_4$	70.6	103.8
Potassium	K_2SO_4	6.85	24.1
Sulfuric acid	H_2SO_4	∞	∞
Potassium alum	$Al_2(SO_4)_3 \cdot 24H_2O$ + K_2SO_4	11.4	∞
Ammonium alum	$Al_2(SO_4)_3 \cdot 24H_2O$ + $(NH_4)_2SO_4$	15	∞
Chlorides			
Calcium	$CaCl_2 \cdot H_2O$	76.8	249
Aluminum	$AlCl_3 \cdot 6H_2O$	69.9	s.d.
Ammonium	NH_4Cl	29.7	75.8
Potassium	KCl	34.7	56.7
Barium	$BaCl_2 \cdot 2H_2O$	31	59
Magnesium	$MgCl_2 \cdot 6H_2O$	167	367
Sodium	NaCl	35.7	39.8
Hydrochloric acid	HCl	∞	∞
Sodium aluminate	$NaAlO_2$	s.	v. s.
Sodium nitrite	$NaNO_2$	72.0	163
Zinc oxide	ZnO	0.00016	0.00016

∞ = soluble in all proportions.
s. = soluble.
d. = decomposes.
v. s. = very soluble.

* C. D. Hodgman (editor), Handbook of Chemistry and Physics, 23rd ed., pp. 350–475. Chemical Rubber Publishing Co., Cleveland, Ohio (1937); *Ceram. Abs.*, **19** [5] 127 (1940).

IV. Data

Table I lists the electrolytes used with their chemical composition and solubility in water.

The results of soluble salt determinations on the mill liquors of the two base frits, milled with no electrolytes,

TABLE II

SOLUBLE SALTS IN MILL LIQUOR

Enamel	Na_2O (gm./l.)	B_2O_3 (gm./l.)	$Na_2O:B_2O_3$ ratio	Excess Na_2O
A (fresh)	0.8491	0.6858	1.24	0.5062
A (aged)	1.385	0.9707	1.43	0.8997
B (fresh)	1.226	0.9672	1.27	0.7454
B (aged)	1.882	1.358	1.39	1.203

TABLE III

SOXHLET EXTRACTIONS OF FRIT

Frit	Na_2O (gm./l.)	B_2O_3 (gm./l.)	$Na_2O:B_2O_3$ ratio	Excess Na_2O	Total solids
A	0.3147	0.1934	1.63	0.2180	1.48
B	0.6294	0.3517	1.79	0.4535	3.10

slips before they were used and their workability during spraying.

No difference in acid resistance was noted except that the enamels which scummed showed a stain in every case, the amount of stain being proportional to the extent of the scumming.

Tables VI and VII show other variations, studied to check the results obtained in the general tests.

The water content of the mills, which contained frit B with the regular mill additions of 6 oz. each of magnesium carbonate and ammonium carbonate, was set at 30, 35, and 40% of the frit. Plates sprayed from the first two mills did not pit, but those from the last mill showed pitting.

As an additional check, the acid-resisting enamel was applied at 40, 50, and 60 gm. per sq. ft. At the regular application weight of 25 to 28 gm. per sq. ft., the enamel pitted, but this defect was eliminated with heavier application weights. All of the enamels that were "short" showed orange peel, but this defect was eliminated as the set was decreased.

V. Discussion of Results

(1) Extraction Data

Both of the frits have a high soluble salt content as shown by the data in Tables II and III. Frit B has a greater amount of these salts present in the extraction and in the mill liquor than frit A. The largest percentage of these salts are alkalis as shown by the Na_2O content, and these excess alkalis in stainless enamels cause the troubles encountered in obtaining proper

TABLE IV

ENAMEL A

	Electrolyte added to mill				Electrolyte added to milled enamel			
	Fresh		Aged		Fresh		Aged	
Electrolyte	Set*	Defects†	Set*	Defects†	Set*	Defects†	Set*	Defects†
Carbonates								
Magnesium (light)	4+	Sl. Sc.	4+	Sc.				
Ammonium	3−	O.K.	3−	Sl. Sc.	3−	O.K.	3−	O.K.
Potassium	3−	"	3−	"	3−	"	3−	"
Calcium	4	B. Sc.	4	B. Sc.				
Sodium	4+	Sl. Sc.	4+	Sc.				
Barium	4	B. Sc.	4	B. Sc.				
Sulfates								
Magnesium (Epsom salts)	2−	O.K.	3+	O.K.	2−	Sh.	3+	Sh.
Ammonium	3+	"	3	Sl. Sc.	3+	O.K.	3	"
Potassium	3	Sl. Sh.	3−	"	3	Sl. Sh.	3	Sl. Sh.
Sulfuric acid	2−	O.K.	2−	O.K.	2−	" "	3+	Sh.
Potassium alum	3+	"	3	"	3+	O.K.	3	O.K.
Ammonium alum	3+	"	3	"	3+	"	3	Sl. Sh.
Calcium	1	"	1	"	1	"	1	O.K.
Aluminum	1−	"	1−	"	1−	"	1−	"
Chlorides								
Ammonium	3	"	3	"	3	"	3	"
Potassium	3	"	3−	Sl. Sc.	3	"	3	"
Barium	2	"	2	O.K.	2	"	2	"
Magnesium	3+	"	3	"	3+	"	3	"
Sodium	3−	"	3−	Sl. Sc.	3−	"	3−	"
Hydrochloric acid	2	"	2−	O.K.	2	"	2−	"
Sodium aluminate	3	"	3	"	3	"	3	"
Sodium nitrite	3−	Sl. Sc.	3−	Sc.	3−	"	3−	"
Zinc oxide	4	B. Sc.	4	B. Sc.				

* Set ratings: 1, short; 2, good; 3, fair; 4, poor.
† Abbreviations: V., very; Sl., slight; B., bad; Sc., scummed; Sh., shorelined; Pit., pitted.

TABLE V

ENAMEL B

	Electrolyte added to mill				Electrolyte added to milled enamel			
	Fresh		Aged		Fresh		Aged	
Electrolyte	Set*	Defects†	Set*	Defects†	Set*	Defects†	Set*	Defects†
Carbonates								
Magnesium (light)	3−	Sl. Sc.	4+	Sc.				
Ammonium	3−	Pit.	3−	"	3−	Pit.	3−	Sc.
Potassium	3−	Sl. Sc.	3−	Sc., Pit.	3−	"	3−	Pit.
Calcium	4	B. Sc.	4	B. Sc.				
Sodium	3−	Sl. Sc., Pit.	4+	Sc., Pit.				
Barium	4	B. Sc.	4	B. Sc.				
Sulfates								
Magnesium	3+	Sh.	3	Sh.	3+	Sh.	3	Sh.
Ammonium	3+	Sl. Sh.	3	Sl. Sc., Sh.	3+	Sl. Sh.	3	Sl. Sh.
Potassium	3	Sh., Sl. Sc.	3−	Sc., Sl. Sh.	3	Sh.	3	Sh.
Sulfuric acid	2−	Sh.	2−	Sh.	2−	"	2−	"
Potassium alum	2−	"	3+	"	2−	"	3+	"
Ammonium alum	2−	"	3+	"	2−	"	3+	"
Calcium	1	V. Sl. Pit.	1	Sl. Pit.	1	O.K.	1	O.K.
Aluminum	1	" " "	1−	Rough surface	1	V. Sl. Pit.	1−	Rough surface
Chlorides								
Ammonium	3+	Pit.	3	Sl. Sc.	3+	Sl. Pit.	3	Pit.
Potassium	3+	Sl. Pit.	3	" "	3+	" "	3	"
Barium	1	V. Sl. Pit.	1	V. Sl. Pit.	1	V. Sl. Pit.	1−	V. Sl. Pit.
Magnesium	2−	Sl. Pit.	3+	Sl. Sc.	2−	Pit.	2−	Sl. Pit.
Sodium	3	" "	3−	" "	3	Sl. Pit.	3	Pit.
Hydrochloric acid	2	Pit.	2	Pit.	2	Pit.	2	"
Sodium aluminate	3+	Sl. Pit.	3	V. Sl. Pit.	3+	V. Sl. Pit.	3	"
Sodium nitrite	3	Sl. Sc.	3−	Sc.	3	Sl. Pit.	3	Sl. Pit.
Zinc oxide	4	B. Sc.	4	B. Sc.				

* Set ratings: 1, short; 2, good; 3, fair; 4, poor.
† Abbreviations: V., very; Sl., slight; B., bad; Sc., scummed; Sh., shorelined; Pit., pitted.

set. They deflocculate the clay particles, thereby causing them to subdivide into small particles which will no longer suspend the frit in the slip. The frit particles settle out and the clay remains in suspension in the supernatant liquid, giving the liquid a muddy appearance. When the ratio of soda to boric oxide is more favorable in the regular superopaque enamels, this deflocculation does not occur, and the supernatant liquid is clear because the clay particles are flocculated. In the case of any settling, the particles settle with the frit, giving a homogeneous mass of frit and clay which is easily brought into suspension by slight agitation.

(2) Action of Electrolytes

The two general types of electrolytes used in this investigation were the easily soluble salts and the slightly soluble salts. In most cases, the slightly soluble salts, namely, barium carbonate, calcium carbonate, and zinc oxide, had no effect on setting up the enamels. Another electrolyte, however, of this type, i.e., magnesium carbonate (light), was effective in setting up the enamels. The magnesium carbonate, which is used in the enamel industry as a set-up agent, is a combination of the carbonate and hydroxide rather than a pure carbonate. The salt is a light fluffy mate-

TABLE VI

ENAMEL A, ELECTROLYTES ADDED TO MILL IN ALL CASES

Electrolytes	Amount*	Fresh enamel		Aged enamel	
		Set†	Defects	Set†	Defects
Potassium carbonate	12	3+	O.K.	3	O.K.
Ammonium chloride	12	2	"	2	"
Ammonium sulfate	12	2−	"	2−	"
Ammonium carbonate	8	3	"	3	"
Ammonium chloride	8	2−	"	2−	"
Ammonium sulfate	8	3+	"	3+	"
Potassium carbonate	8	3	"	3	"
Potassium sulfate	8	3	"	3	"
Potassium chloride	8	3+	"	3+	"
Calcium chloride	2	2+	"	2+	"
Magnesium carbonate	6		Sl. orange peel		
Calcium chloride	1	2	O.K.	2	"
Magnesium carbonate	5				

* Amount given in ounces added per 100 lb. of frit.
† Set ratings: 2, good; 3, fair.

TABLE VII

ENAMEL B, ALL ELECTROLYTES ADDED TO MILL

Electrolytes	Amount added (oz./100 lb.)	Sp. gr.	Remarks
Potassium alum	1	1.80	No pits; shoreline
" "	2	1.80	" " "
" "	3	1.80	" " "
" "	6	1.80	O.K.; enamel "short"
" "	8	1.80	O.K.; enamel "very short"
" "	8	1.68	Shorelines
" "	3		
Magnesium carbonate	4	1.80	Shorelines; good set
Potassium alum	3		
Aluminate	4	1.80	" " "
Potassium alum	4		
Magnesium carbonate	4	1.80	Sl. shoreline
Potassium alum	4		
Aluminate	4	1.80	" "
Ammonium sulfate	8	1.80	O.K.
Magnesium carbonate	5		
Ammonium "	5	1.80	Pit.; fair set
Magnesium "	6		
Ammonium "	6	1.80	Pit.
Magnesium "	7		
Ammonium "	7	1.80	"
Magnesium "	8		
Ammonium "	8	1.80	Pit.; good set
Magnesium "	8		
Ammonium "	8	1.87	O.K.
Magnesium "	8		
Ammonium "	8	1.72	Pit.
Magnesium "	8		
Ammonium "	8	1.63	"
Magnesium "	5	1.80	
Ammonium "	5		
Potassium alum	1		Shoreline
Magnesium carbonate	5		
Ammonium "	5		
Potassium alum	2	1.80	"

rial, formed by the precipitation of magnesium carbonate, but during this process some of the carbonate hydrolyzes to give the hydroxide. When this basic carbonate is added to water, it remains in suspension and retards the settling of the frit particles.

The soluble electrolytes may react with the clay and cause a flocculation. The electrolytes and the soluble salts may also react to give other soluble salts which do not affect the properties of the enamel slip.

(3) Effect of Electrolytes on Set

The tested electrolytes may be classed in three general groups, viz., carbonates, sulfates, and chlorides. The chlorides as a group gave the best set, the sulfates were intermediate, and the carbonates were the least effective. This classification was apparent after check tests were made on the entire group of electrolytes, but for additional proof the enamels, listed in Table VI, were prepared. There was a greater difference between the enamels with a larger addition of electrolyte. The carbonates had fair set, but the enamel had a tendency to be runny; the sulfates had good set; and the chlorides were almost short. These data show that the type of anion has a definite effect on the set resulting from the electrolyte addition.

The cation present was also a controlling factor in the development of set. The tests with the monovalent salts showed the order of decreasing effect to be H^+, NH^+_4, K^+, and Na^+. With the divalent salts, the order was Ca^{++}, Ba^{++}, and Mg^{++}; the difference, however, was not as great as with the monovalent salts, possibly because all of these salts are hydrates and the actual amount of anion and cation added would vary somewhat.

The addition of the electrolyte to the milled enamel seemed to give a higher initial set, but there was little difference between the aged enamels whether the electrolyte was added to the mill or to the milled enamel. It was difficult to add the electrolyte and to mix it thoroughly with the milled enamel, which perhaps accounts for the seemingly high initial set.

(4) Scumming

The scumming encountered in this study was a typical underfire scum which could be eliminated on extended firing. The enamels containing additions of calcium carbonate, barium carbonate, and zinc oxide had poor set, and all scummed badly both with the fresh and the aged enamels. The other carbonates and sodium nitrite showed a slight scumming with the fresh enamel, and the scumming increased as the enamel was aged. Other enamels, on the borderline between poor and fair set, scummed when they were aged. These enamels, however, did not scum when the electrolytes were added to the milled enamel.

No scumming could be traced to the presence of sulfates or chlorides in the mill addition.

(5) Shorelines

Shorelines were encountered in both frits, but the tendency was greater in frit B than in frit A. The greater soluble salt content of frit B may account for its increased shorelining tendency.

Shorelines probably are caused by the precipitation of soluble salts during drying, but there are no indications of the lines on the dried piece. Drying conditions do not explain the difference in shorelining tendencies in this investigation because all of the test plates were dried under the same conditions.

In this study, shorelining occurred only when electrolytes containing the sulfate radical were used, which indicates that the presence of sulfate is necessary. The defect was eliminated, however, by adding more of the same electrolyte which caused the enamel to be "short." This increase in set at first was thought to be the controlling factor, but reducing the amount of sulfate and adding some other electrolyte to a point where the enamel was again "short" did not eliminate this defect. The enamel, which contained 8 oz. of alum was "short," but no shorelines occurred when it was sprayed at a specific gravity of 1.80. When this same enamel, however, was sprayed at a specific gravity of 1.68, shorelines appeared on the fired piece.

From these results, it seems that a combination of factors, rather than only one, causes this defect, viz., (1) the soluble salts in the mill liquor as controlled by the solubility of the frit, (2) the electrolyte used, and (3) the set of the enamel.

(6) Pitting

Pitting was troublesome only when frit B was used, and the sulfates were the only electrolytes which would eliminate this defect. The frit with the high soluble salt content again caused the trouble. This defect possibly is caused by the fluxing action of the soluble salts which probably are deposited during drying. These salts fire down faster than the enamel itself, and pits or depressions are formed in the enamel surface. The enamel milled with no electrolyte scummed over practically the entire surface of the plate, but there were some glossy spots. On extended firing, the pits appeared near these glossy areas.

Set had some effect on this defect because the enamels with too much set seemed to give less pitting than the other enamels. Aging seemed to have no appreciable effect on increase in pitting. Pitting was also eliminated by spraying the enamel in a heavier coating.

(7) Acid Resistance

The only noticeable effect on the acid resistance was the staining which was encountered when the enamel had poor set. The staining was eliminated by increasing the electrolyte to the point where proper set was obtainable. The addition of 12 oz. of sulfates, 12 oz. of chlorides, and 16 oz. of the carbonates per 100 lb. of frit did not cause the enamels to stain. From these data, it may be said that none of the electrolytes tested affected the acid resistance as long as the set was within reasonable limits.

(8) Defects Eliminated in Plant Operation by Variations in Electrolytes

Pitting was encountered when a stainless enamel was used in regular production. The problem was brought

into the laboratory, and the results obtained in this study were applied. The addition of alum eliminated the pitting, but shorelines were formed. The shorelines were eliminated when the alum was decreased and sodium aluminate was added. The shorelining tendency of this enamel was not as great as in frit B.

"Chicken skin," a defect produced in some acid-resisting enamels, is characterized by a crinkly appearance of the enameled surface after firing, but it is not apparent when the unfired ware is inspected. This defect was more evident in the laboratory when the set of the enamel was poor. Improving the set with the addition of more electrolyte removed the defect.

These results were verified in regular plant operation, and the defect was eliminated in future runs of the enamel.

VI. Conclusions

(1) The set obtained in an enamel by the addition of an electrolyte is influenced by (*a*) the type of anion added (Cl^-, SO_4^{--}, and CO_3^{--}), (*b*) the added cation (H^+, NH_4^+, K^+, Na^+, etc.), and (*c*) the valency of the added cation (Na^+, Ca^{++}, etc.).

(2) The scumming tendency increases as set decreases.

(3) Aging increases the scumming tendency.

(4) Shorelines are caused by a combination of factors which include soluble salts in the mill liquor controlled by the solubility of the frit used, the kind and amount of electrolyte added, and the set of the enamel.

(5) Sulfates or salts that contain the sulfate radical are one factor which contributes to the shorelines in the enamels studied.

(6) None of the electrolytes in the amounts used contributes to pitting.

(7) Pitting may be eliminated by increasing the specific gravity of the enamel, by the addition of sulfates, or by heavier application.

(8) The type and amount of electrolyte added in order to obtain good set does not affect the acid resistance of the enamel.

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EFFECT OF VARIOUS CATALYSTS ON CONVERSION OF QUARTZ TO CRISTOBALITE AND TRIDYMITE AT HIGH TEMPERATURES*

By Nelson W. Taylor and Cho-Yuan Lin

Abstract and Summary

The action of a considerable number of pure oxides, fluorides, chlorides, borates, phosphates, carbonates, and other compounds and of certain mixtures, as well as the effect of several minerals in promoting or accelerating the inversion of quartz to cristobalite and tridymite at temperatures between 1000° and 1500°C. has been studied. Alkali oxides are found to be superior to all other substances, and they are effective in amounts of less than 0.1%. Acid oxides, such as B_2O_3 or P_2O_5, seem to have little or no value as catalysts for this inversion. Possible mechanisms for the inversion process are presented, and some applications of controlled inversion in the heat treatment of ceramic bodies are mentioned. A few data are also given on the temperature of the "low-high" change in cristobalite.

I. Introduction

The sluggish character of the inversion of quartz to cristobalite and tridymite is well known. Although quartz is unstable in its relation to tridymite above 870°C., if it is pure it may be heated for a long time at much higher temperatures without appreciable conversion. If change does occur, cristobalite is usually the first product to be formed.

The object of this investigation was to examine the influence of various substances, added in small amounts, on the rate of the inversion process. The information may be of value in itself and also in providing the basis for a general theory applicable to the catalytic inversion of polymorphic oxides other than silica. From a strictly practical viewpoint, a knowledge of how to

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effect structural changes in silica with greater speed is important in the manufacture of silica brick and whiteware and, in fact, for all ceramic products which have free silica, in one form or another, as a constituent.

(1) Previous Work on the Subject

A survey of the literature[1] dealing with the effect of added substances on the efficiency of quartz conversion yielded about forty references which covered the period since 1899. The details of these earlier studies will not be given here. It is often difficult to judge critically the results of some of the authors, to compare one with another, or to explain the contradictions here and there encountered because, in most of the papers, no exact description is given of the quartzite used. In many cases, small traces of impurities occurring naturally in the quartz played an important role and frequently masked or disturbed the effect of the added reagent.

(2) Materials and Experimental Procedure

A quantity of "glass sand," from the Oriskany formation at Mapleton, Pa., was milled and screened to yield a 150- to 200-mesh product. This was treated five or six times in boiling concentrated hydrochloric acid until the acid was colorless. After the silica was washed in distilled water until free from acid and dried in an electric oven, it was ready for use. The purity of the silica sample was confirmed by evaporation with hydrogen fluoride in a platinum crucible. The silica was completely evaporated, leaving no stain or residue.

The "catalytic" reagents, which were commercial chemicals of c.p. grade unless otherwise noted, were passed through a 200-mesh sieve before being mixed with the silica.

Five grams of the purified silica were weighed out with the proper amount of catalyst and were mixed intimately. A few drops of 2% dextrin solution were added as a binder, and the mixture was pressed into the form of a small cylinder and dried. The specimens were fired, either in an electric furnace or in a gas-fired furnace, for a definite temperature and time. After firing, they were examined visually or with low-power binoculars for evidence of sintering and then crushed to pass a 140-mesh sieve. No attempt was made to remove the catalyst from the silica before determining the density, but the error thus introduced cannot be large as the amount of catalyst used was 2% or less.

Densities of the powder were determined by the vacuum pycnometer technique, i.e., heating the sample to 200°C. under vacuum and using tetralin ($C_{10}H_{12}$) as the displacement liquid. Check results agreed to 1 or 2 units in the third decimal.

[1] Cf. also R. B. Sosman, Properties of Silica. Chemical Catalog Co., Inc., New York, N. Y., 1927; *Ceram. Abs.*, 7 [7] 505 (1928).

II. Experimental Results

(1) Effect of Lime

In view of the wide use of lime as an addition agent in silica brick, the data given in Table I may be of interest.

The density of quartz, cristobalite, and tridymite at ordinary temperatures is, respectively, 2.65, 2.33, and 2.27. The lower the density of the product, therefore, the greater is the degree of conversion of the quartz to cristobalite and tridymite. It is not possible to compute the percentage of each from the density for all three phases are present in many cases. If, however, the density is less than 2.33, there must be a substantial percentage of tridymite in the sample, and if the density is above 2.50, at least 53% of quartz must be present.

(2) Effect of Various Substances at 1000°C.

Calcium oxide had no converting effect on quartz

TABLE I

EFFECT OF CaO ON INVERSION OF QUARTZ

CaO by weight (%)	Firing conditions			Character of product	
	°C.	Hr.	Furnace	Texture	Density (gm./cc.)
2	1000	2	Electric	Loose	2.65
2	1300	2	Gas, reducing atmosphere	"	2.62
2	1350	2	" " "	Sintered	2.54
2	1450	2	" " "	"	2.35, 2.33
0.5	1500	2	" " "	Loose	2.54
0.1	1450	4	" " "	"	2.33
0.2	1450	4	" " "	"	2.32
0.5	1450	4	" " "	"	2.32
1.0	1450	4	" " "	Sintered	2.34

TABLE II

DENSITY OF SILICA WITH 2% BY WEIGHT OF CATALYST (Fired 2 Hr. at 1000°C.)

Catalyst	Mols of catalyst/ 100-gm. batch	Density (gm./cc.)	Texture	Eutectic temp. (°C.) (catalyst + SiO_2)
Li_2CO_3	0.027	2.45	Sintered	1028
Na_2CO_3	.019	2.47	"	793
K_2CO_3	.014	2.56	"	752
BeO	.080	2.65	Loose	
MgO	.050	2.65	"	1543
CaO	.036	2.65	"	1436
$Sr(NO_3)_2$	.012	2.66	"	1358 (SrO)
$BaCO_3$	.010	2.62	"	1370
LiF	.038	2.44	Sintered	
NaF	.024	2.45	"	
$KF \cdot 2H_2O$	.011	2.62	"	
CaF_2	.025	2.64	Loose	
$Ca_3(PO_4)_2$	.006	2.65	"	
Na_2HPO_4	.009	2.63	"	
NaCl	.017	2.60	"	
$CaCl_2$	.018	2.63	"	

when it was fired for 2 hours at 1000°C. In order to see whether other substances might be active under these conditions, a number of trials were made which are recorded in Table II.

The carbonates and fluorides of lithium, sodium, and potassium are all effective to some degree in promoting the inversion of quartz. The potassium compounds appear to be the least active. The lithium salts have somewhat greater influence than the sodium salts, although if equal numbers of mols had been used, the sodium carbonate and fluoride probably would rank definitely first. The phenomenon of sintering appears (from Table II) to correlate with the degree of inversion as measured by the density, but it will be shown later that this is purely a coincidence. The sintering is regarded as being caused by the formation of a liquid phase at some time during the firing process, although some sintering may result purely from grain growth or from solid phase reaction. Sintering is desirable in the manufacture of silica brick in order to give strength.

Table II gives some evidence of the role of fluorides in promoting the inversion of quartz at 1000°C. The lithium carbonate with its 19% of Li is just about as effective as the lithium fluoride with its 27% of Li (the percentages are calculated on the basis of atomic weights). The sodium carbonate with 43% of Na, similarly, is about as effective as the sodium fluoride with 55% of Na. It had been thought that the fluorides would possibly promote the quartz inversion by forming SiF_4 or some complex fluosilicate as an intermediate step, but the present evidence seems to indicate that the alkali ion is the effective agent. Further data will bear out this conclusion.

(3) Effects at 1300°C.

Table III presents data based on 2 hours of firing at 1300°C. in a gas-fired furnace under reducing conditions. This series deals with the role of CaO, Fe_2O_3, and mixtures of these with certain fluorides.

In evaluating the percentage of conversion as shown in Table III, the calculation is made on the assumption that a conversion from 2.65 to 2.27 represents 100%, i.e., the problem is treated as if the only solid phases present were quartz and tridymite.

Table III brings out the interesting point that iron oxide is more effective than lime in promoting the inversion of quartz and also that it produces a stronger product. Iron oxide has, in fact, been used commercially, and it is regarded as a satisfactory reagent, provided the color of the resulting brick is not objectionable. The effect of adding fluorides and alkalis in the form of NaF or Na_3AlF_6 is clearly shown. Fluoride, in the form of CaF_2, does not seem to be particularly effective. The effect of increasing the amount of the catalyst on the degree of conversion is clearly shown in several cases; e.g., when the amount of cryolite is increased from 0.1 to 0.5%, the density of the fired silica is lowered from 2.60 to 2.39. This is probably to be ascribed to the more effective coating of the surfaces of the quartz grains and therefore to the increased probability of chemical action at these surfaces. The increase in the degree of sintering also indicates the presence of more liquid, but the absolute amount of liquid present must be small in any case, probably not more than a very thin film. The observed activity of sodium silicate confirms the statements of other investigators, particularly that of Cole,[2] although he worked at lower temperatures.

(4) Effects at 1350°C.

The data obtained from a few tests made at 1350°C. are presented in Table IV, which shows that 2% of CaO and 2% of Fe_2O_3 are equally effective at 1350°C. The iron oxide was more active than the lime at 1300°C. as shown in Table III. The action of both of these oxides is improved by the addition of sodium carbonate, and a well-sintered product with a density of only 2.34 was obtained when a mixture of 2 gm. of CaO and 0.5 gm. of Na_2CO_3 per 100 gm. of quartz was used.

TABLE III

DENSITY OF SILICA FIRED UNDER REDUCING CONDITIONS
(2 Hr. at 1300°C. in Gas-Fired Furnace)

Catalyst (%)	Density	Conversion (%)	Texture
No catalyst	2.64	3	Loose
CaO 2	2.62	8	"
" 2, NaF 0.2	2.43	58	Slightly sintered
" 2, NaF 0.5	2.39	69	Sintered
" 2, CaF_2, 0.5	2.58	18	Slightly sintered
" 2, cryolite 0.2	2.49	42	" "
" 2, cryolite 0.5	2.44	55	Sintered
NaF 0.1	2.46	50	Loose
" 0.2	2.36	76	"
" 0.5	2.33	84	Slightly sintered
Fe_2O_3 2	2.55	26	Sintered
" 2, NaF 0.2	2.49	42	"
" 2, NaF 0.5	2.44	55	"
" 2, cryolite 0.2	2.50	39	"
" 2, cryolite 0.5	2.46	50	"
Cryolite 0.1	2.60	13	Loose
" 0.2	2.54	29	Slightly sintered
" 0.5	2.39	69	Sintered
NaF 1	2.31	90	"
*Sodium silicate 0.5	2.56	24	Loose
" " 1.0	2.37	74	"
" " 2.0	2.33	84	"
Na_2CO_3 0.5	2.33	84	"

* Sodium silicate is the S brand of the Philadelphia Quartz Co.

TABLE IV

DENSITY OF SILICA FIRED UNDER REDUCING CONDITIONS
(2 Hr. at 1350°C. in Gas-Fired Furnace)

Catalyst (%)	Density	Conversion (%)	Texture
No catalyst	2.60	13	Loose powder
CaO 2	2.54	29	Sintered
" 2, Na_2CO_3, 0.5	2.34	82	"
Fe_2O_3 2	2.54	29	"
" 2, Na_2CO_3 0.5	2.46	41	"

(5) Effects at 1450°C.

(*A*) *Various Catalysts:* An extensive series of tests

[2] S. S. Cole, "Conversion of Quartz into Cristobalite below 1000°C. and Some Properties of Cristobalite Formed," *Jour. Amer. Ceram. Soc.*, **18** [5] 149–54 (1935).

using different reagents was made at 1450°C. Table V compares the results with alkali compounds (having univalent cations) with those due to alkaline earth compounds. The amount of catalyst added in each case was 2% by weight, except that of the phosphoric acid addition in which 1 cc. of H_3PO_4 (concentrated) was used with 5 gm. of SiO_2.

Compounds of univalent cations, i.e., those of Li, Na, and K, give a high degree of conversion of quartz at 1450°C. The density is less than 2.33 in many cases, indicating that probably all of the quartz has disappeared and that the product is a mixture of cristobalite and tridymite. A sample of quartz without a catalyst gave a density of 2.50. Phosphoric acid or its anhydride, P_2O_5, actually inhibits even this degree of conversion because the density of the silica is higher than 2.50 when the phosphorus compound is present. The TiO_2 also appears to have a strong inhibiting effect. Tribarium aluminate, $3BaO \cdot Al_2O_3$, is another interesting compound which has been proposed as a substitute for CaO in the manufacture of silica brick. Table V, however, shows that it is not nearly so effective as CaO in promoting structure changes in silica. It appears in fact to inhibit such change as pure quartz itself will undergo at 1450°. It does, however, produce some sintering. The effect of phosphate also seems to be unimportant. Calcium oxide and $CaCO_3$ are more active. The action of the calcium phosphate is probably due to its CaO content and that of sodium phosphate to its soda content. Barium carbonate is the most active of the alkaline earth series, which may be due to the fact that BaO, in its relations with SiO_2, behaves more like the alkali oxides than BeO, MgO, CaO, or SrO.[3] Although the last-named oxides form two liquid phases with silica, the BaO forms a single homogeneous liquid which will form in small amounts (but sufficiently large) to act as a temporary solvent for quartz and to promote the change to cristobalite or tridymite at all temperatures above the eutectic, 1370°C. The most active of the three iron compounds is Fe_2O_3, which has the highest percentage of FeO (under reducing conditions), so that probably the degree of conversion of the quartz is determined here by the amount of FeO present during the firing process.

Carbon black was thought to be a possible catalyst for the conversion of quartz on the theory that it might reduce the quartz to free silicon which would subsequently oxidize to cristobalite. The density of silica

[3] For example, see F. C. Kracek, "Cristobalite Liquidus in Alkali Oxide–Silica Systems and Heat of Fusion of Cristobalite," *Jour. Amer. Chem. Soc.*, **52** [4] 1436–42 (1930); *Ceram. Abs.*, **9** [9] 783 (1930).

TABLE V

DENSITY OF SILICA FIRED UNDER REDUCING CONDITIONS

(2 Hr. at 1450°C. in Gas-Fired Furnace)

Catalyst	Density	Catalyst	Density	Catalyst	Density
Li_2CO_3	2.31	BeO	2.41	$FeSO_4$	2.47
Na_2CO_3	2.32	MgO	2.50	Fe_2O_3	2.43
K_2CO_3	2.29	CaO	2.35	$FeSO_4 \cdot (NH_4)_2SO_4$	2.51
LiF	2.34	$CaCO_3$	2.41		
NaF	2.32	$Sr(NO_3)_2$	2.43	TiO_2	2.65
$KF \cdot 2H_2O$	2.33	$BaCO_3$	2.34	B_2O_3	2.48
LiCl	2.32	$MgCl_2$	2.42	H_3PO_4	2.53
NaCl	2.33	CaF_2	2.37	No catalyst	2.50
KCl	2.34	$CaCl_2$	2.38	C (black)	2.53
Na_2HPO_4	2.31	$BaCl_2$	2.40	Al (powder)	2.62
$Na_2WO_4 \cdot 2H_2O$	2.32	$Ca_3(PO_4)_2$	2.44		
$Na_2MoO_4 \cdot 2H_2O$	2.32	$3BaO \cdot Al_2O_3$	2.60		
Density range	2.29–2.34	Density range	2.34–2.60	Density range	2.43–2.65

TABLE VI

DENSITY OF SILICA FIRED UNDER REDUCING CONDITIONS WITH 2% ADDITIONS (DENSITY, WITHOUT CATALYST, 2.50)

(2 Hr. at 1450°C. in Gas-Fired Furnace)

Iron-containing compounds		Phosphates		Boron compounds		Fluorine compounds	
Eudialyte	2.35	Apatite	2.51	Ulexite	2.34	Thomsenolite	2.37
Jarosite	2.36	Collophanite	2.56	Howlite	2.42	Cryolite	2.32
Biotite	2.52	Autunite	2.56	Camsellite	2.45	Gearksutite	2.57
Staurolite	2.58	Amblygonite	2.55	Dumortierite	2.61	Chrondrodite	2.55
Chromite	2.47	Wavellite	2.62	Colemanite	2.51	Amblygonite	2.55
Goethite	2.42	Monazite	2.63	Vonsenite	2.46	Apatite	2.51
Magnetite	2.49	$Ca_3(PO_4)_2$	2.44	Tourmaline	2.58	Vesuvianite	2.50
Ilmenite	2.47	Na_2HPO_4	2.31	Datolite	2.53		
Allanite	2.48	H_3PO_4	2.53	B_2O_3	2.48		
Ferrimolybdite	2.56						
Vonsenite	2.46						
Almandite garnet	2.41						
Fe_2O_3	2.43						
$FeSO_4 \cdot 7H_2O$	2.47						
Ferrous ammonium sulfate	2.51						
Fe_2O_3 (1%) with beryl (1%)	2.43						

produced in this test was 2.53 gm. per cc. As this is higher than 2.50 (the density obtained when no catalyst was used), it must be concluded that, under these conditions at least, the carbon black acts to inhibit rather than to accelerate the structure change of the quartz. Mixtures of carbon black with other reagents were also inactive.

(*B*) *Action of Certain Minerals:* No attempt was made to refine or purify the minerals used in these tests; they were simply the best samples obtainable from a commercial supply house. The results are shown in Table VI.

The action of sixteen iron-containing minerals was tried in the 2-hour firing at 1450°C. The only minerals producing a density of less than 2.40 were eudialyte, Na_{13} (Ca, Fe)$_6$Cl (Si, Zr)$_{29}O_{82}$, with a density of 2.35, and jarosite, $K_2Fe_6(OH)_2(SO_4)_4$, with a density of 2.36. The catalytic effect in these cases was due to the Na or K which was present in these minerals.

Similar remarks may be made about a group of nine phosphates; the only one leading to a density of less than 2.40 was Na_2HPO_4, which gave a density of 2.31 gm. per cc.

Eight boron minerals were also tested. All of the final densities were above 2.40 except ulexite, $NaCaB_5O_9 \cdot 8H_2O$, which showed 2.34. The effect again is ascribed to the sodium content of this mineral.

A series of seven fluorine-containing minerals was tested, but the only ones leading to densities of the silica of less than 2.50 were thomsenolite, $NaF \cdot CaF_2 \cdot AlF_3 \cdot H_2O$, 2.37 and cryolite, Na_3AlF_6, 2.32. These low values are also to be attributed to the sodium content of the minerals.

These studies show that alkali oxides, such as Li_2O, Na_2O, or K_2O, are superior to the acid oxides, P_2O_5 or B_2O_3, or to fluorides in promoting this silica inversion.

(*C*) *Sintering:* Observations made on the texture of the product after firing confirm the statement made earlier in this paper that sintering, i.e., cementing together of the grains to produce a strong mass, does not necessarily indicate a high degree of quartz inversion to cristobalite and tridymite. This is illustrated by data given in Table VII.

TABLE VII

REAGENTS PRODUCING POOR CONVERSION BUT GOOD SINTERING OF SILICA AND VICE VERSA

Catalyst (2%)	Density	Texture
No catalyst	2.50	Loose
Gearksutite, CaF_2Al (F, OH)$_3 \cdot H_2O$	2.57	Sintered
Biotite, $(H \cdot K)_2(Mg, Fe)_2Al_2(SiO_4)_3$	2.52	"
Vesuvianite, $Ca_6(OH, F)Al_3(SiO_4)_5$	2.50	"
Muscovite, (H_2K) $(AlSiO_4)_3$	2.58	"
H_3PO_4	2.53	"
$3BaO \cdot Al_2O_3$	2.60	"
Trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	2.32	Loose
Ulexite, $NaCaB_5O_9 \cdot 8H_2O$	2.34	"
Lepidolite, $(OH, F)_2KLiAl_2Si_2O_{10}$	2.38	"

These data show that a number of substances, which actually inhibit the quartz inversion, nevertheless tend to bond or cement the grains and that certain other substances which are quite good catalysts for promoting the cristobalite and tridymite formation, yield a loose and unconsolidated powder. Each of these classes of substances in its own way may be valuable in whiteware bodies or in other ceramic products.

(*D*) *Amount of Catalyst:* A study was made at 1450°C. with the amount of catalyst ranging from 0.1 to 2%. The firing time again was 2 hours in a gas-fired furnace under reducing conditions. Table VIII, which presents the results, indicates that small amounts of certain catalysts are effective. Only 0.1% of Na_2CO_3 by weight reduces the density of silica to 2.32, and even as little as 0.08% of NaOH reduces the density to 2.30. A product of this density might consist of equal amounts of cristobalite and tridymite without any quartz. Under the same conditions of firing and in the absence of a catalyst, quartz alone shows a density of 2.50, i.e., only about 47% is converted. The effectiveness of NaOH or of Na_2CO_3 is striking and indicates that desirable results may be achieved in a simple and inexpensive manner, as it is necessary only to wet the quartz grains with the sodium hydroxide solution. This could be easily accomplished in the silica refractories and in the whitewares industries. As to the fluxing action of this

TABLE VIII

SILICA DENSITIES WITH DIFFERENT AMOUNTS OF CATALYSTS FIRED UNDER REDUCING ATMOSPHERE

(2 Hr. at 1450°C. in Gas-Fired Furnace)

	0.1%	0.5%	1.0%	2.0%
Li_2CO_3	2.40	2.32	2.32	2.31
Na_2CO_3	2.32	2.33	2.32	2.32
K_2CO_3	2.33	2.36	2.31	2.29
Fe_2O_3	2.44	2.42	2.40	2.43
NaOH	0.4% (5 drops of 10% NaOH sol./5 gm. of SiO_2)			2.31
"	0.08% (1 drop of 10% NaOH sol./5 gm. of SiO_2)			2.30
KOH	0.4% (5 drops of 10% KOH sol./5 gm. of SiO_2)			2.30
"	0.08% (1 drop of 10% KOH sol./5 gm. of SiO_2)			2.33

amount of soda, a simple calculation shows that the silica would contain 0.06% of Na_2O, which would lower the melting point from 1732° to approximately 1730°C. For most practical purposes, this lowering of 1.7° is not serious. The presence of free quartz in whiteware bodies is sometimes the cause of "dunting" or of other defects. These difficulties might be ameliorated or even eliminated and the rate of solution of quartz in the vitreous phase might be accelerated by the addition of small quantities of sodium hydroxide or carbonate solutions to "dry-press" bodies or to bodies which do not ordinarily receive alkaline deflocculating salts.

Tests were made in a 4-hour firing at 1450°C. with various amounts of Na_2CO_3, Na_2WO_4, and Na_2MoO_4 as catalysts. As tungstates and molybdates were used in Fenner's equilibrium studies on the polymorphic forms of silica,[4] the action of these substances in small amounts is interesting (see Table IX). All of the products had a loose powdery texture.

All of these density values lie below 2.33, indicating

[4] C. N. Fenner, "Stability Relations of the Silica Minerals," *Amer. Jour. Sci.*, [4th Series] **36**, 331–84 (1913).

the absence of quartz, i.e., complete conversion to a mixture of cristobalite and tridymite.

(*E*) *Mixed Catalysts:* In an attempt to combine the advantages of a high percentage conversion of quartz and sintering of the product, mixtures of reagents were tried out in 2-hour and 4-hour firings. The results are shown in Tables X and XI. Only those combinations resulting in sintered products are included.

TABLE IX

SILICA DENSITIES WITH DIFFERENT AMOUNTS OF CATALYSTS FIRED UNDER REDUCING ATMOSPHERE

(4 Hr. at 1450°C. in Gas-Fired Furnace)

	0.1%	0.2%	0.5%	1.0%
Na_2CO_3	2.29	2.31	2.31	2.32
Na_2WO_4	2.31	2.30	2.31	2.30
Na_2MoO_4	2.30	2.30	2.30	2.31

TABLE X

SILICA DENSITIES WITH MIXED CATALYSTS FIRED UNDER REDUCING ATMOSPHERE (ALL PRODUCTS SINTERED)

(2 Hr. at 1450°C. in Gas-Fired Furnace)

Catalyst (%)	Density
Fe_2O_3 1, NaOH 0.08	2.43
" 1, NaOH 0.4	2.42
" 2, NaF 0.2	2.29
" 2, NaF 0.5	2.31
" 2, cryolite 0.2	2.35
" 2, cryolite 0.5	2.34
" 1, CaO 1	2.54
" 2	2.43
CaO 2, NaF 0.2	2.33
" 2, cryolite 0.2	2.34
" 2, CaF_2 0.5	2.35
" 2	2.33

TABLE XI

SILICA DENSITIES WITH MIXED CATALYSTS FIRED UNDER REDUCING ATMOSPHERE (ALL PRODUCTS SINTERED)

(4 Hr. at 1450°C. in Gas-Fired Furnace)

Catalyst (%)	Density
CaO 1, Na_2CO_3 0.1	2.32
" 1, Na_2CO_3 0.2	2.31
" 1, Na_2CO_3 0.5	2.34
" 1, Na_2CO_3 1.0	2.33
" 1	2.34
No catalyst (product loose)	2.44

In the first two mixtures in Table X, the sodium hydroxide does not appear to add much to the effectiveness of Fe_2O_3. The sodium fluoride and the cryolite additions, however, show definite improvements over Fe_2O_3 alone. The CaO alone is an effective catalyst at 1450°C.

In the 4-hour firing (Table XI), the addition of 0.2% of Na_2CO_3 to 1% of CaO seems to have a definite advantage over 1% of CaO alone, but the density is not as low as when Na_2CO_3 is used alone. Data on firings of catalytic sintering mixtures at 1300° or 1350°C. would be interesting because CaO is a poor reagent even at 1350°C. (see Table IV).

(*F*) *Test for Presence of Liquid Phase:* The fluorescence test in the presence of a small amount of uranyl nitrate may be used to indicate the presence of a liquid or vitreous phase. Four drops of 10% uranyl nitrate solution were added to 5 gm. each of the mixtures listed in Table XII.

TABLE XII

FLUORESCENCE OF Na_2CO_3-SiO_2 MIXTURES FIRED UNDER REDUCING ATMOSPHERE

(4 Hr. at 1450°C. in Gas-Fired Furnace)

Sample	Fluorescence
SiO_2 + 0.1% Na_2CO_3	None
" " 0.2 "	"
" " 0.5 "	Very weak
" " 1.0 "	Weak
" " 2.0 "	Strong

Inasmuch as fluorescence is a characteristic of glasses rather than of strictly crystalline solids containing uranium, the data in Table XII show that the liquid phase can be detected even when as little as 0.5% of Na_2CO_3 is added to silica and fired at 1450°C. It is not surprising that some liquid phase would develop because the eutectic occurs below 800°C. in this system. Table IX shows, however, that good conversion of quartz is effected at this temperature with only 0.1% of Na_2CO_3 (d = 2.29).

(6) Effects at 1500°C.

A series was made using only 0.5% of the reagent in a 2-hour firing at 1500°C. Table XIII presents the results of these tests. A comparison with Table VIII shows that 0.5% of Na_2CO_3 or of K_2CO_3 is slightly more effective in the conversion of quartz at 1500°C. than at 1450°C.

TABLE XIII

SILICA DENSITIES WITH 0.5% OF REAGENT FIRED UNDER REDUCING CONDITIONS

(2 Hr. at 1500°C. in Gas-Fired Furnace)

Catalyst	Density	Catalyst	Density
CaO	2.54	NaOH	2.32
Fe_2O_3	2.53	KOH	2.31
Na_2CO_3	2.32	No catalyst	2.52
K_2CO_3	2.33		

All products loose powder.

(7) Petrographic Observations

In Table VIII, it was shown that 2% of Li_2CO_3, Na_2CO_3, and K_2CO_3 produced silica densities of 2.31, 2.32, and 2.29, respectively, when the samples were fired 2 hours at 1450°C. All of these products showed beautiful tridymite twins and appeared to consist only of tridymite and cristobalite with no quartz. The refractive index in each case ranged from 1.484 to 1.489. The K_2CO_3 sample showed about 70% of tridymite; each of the other two showed about 50%. The density data are considered to be more useful because it is difficult to determine the exact amount by petrographic examination.

(8) Thermal Expansion in Range of 200° to 300°C.

Thermal-expansion measurements were made on a

number of the products, using a mercury dilatometer, which consisted essentially of a cylindrical reservoir tube of stainless steel, about 0.5 in. inside diameter and 2.5 in. inside length, to which was attached a capillary glass tube of 0.016 sq. cm. inside cross-sectional area. A thermocouple was placed in a well sealed into the reservoir. A weighed sample of silica product was placed in the reservoir, mercury was added to fill it, and the dilatometer was placed in a small electric furnace and heated. The expansion was readily observed by movements of the meniscus along the glass capillary. The expansion was uniform and apparently linear from 170°C. to some temperature at which the anomalous expansion of cristobalite, owing to the $\alpha \rightarrow \beta$ change, began to occur. This temperature is recorded in Table XIV.

No detailed explanation is offered for these effects. The α to β transformation is initiated as low as 220°C. or as high as 253°C. The "catalyst" possibly is taken to some degree into solid solution in the β-cristobalite which formed during the firing operation. There is evidence for this in the well-known close similarity of crystal structures of high cristobalite, α-carnegeite, nepheline, and the feldspars. Further study will be necessary to explain these interesting phenomena. It is clear that not all "cristobalite" is alike but that a variety of cristobalite products can be made with quite widely differing properties, and it may be possible in the future to utilize these differences in ceramic bodies when controlled expansion is desired. Other investigators have reported cristobalite with various inversion temperatures. An extensive summary and discussion of the problem is given by Sosman.[1]

III. Mechanism of Catalytic Process

(1) Liquid Phase Reaction

The transfer of silica from an unstable to a stable form by means of a liquid phase is easy to understand because the unstable crystal form of a solid always has a higher solubility than the stable form. Before the liquid is saturated with quartz, it becomes saturated with cristobalite which crystallizes as fast as the quartz can dissolve. This theory postulates that above 870°C. cristobalite is more stable than quartz. Actually 870° to 1470°C. is the stable range of tridymite toward which the cristobalite formation appears to be the first step. Cristobalite, however, is not known to change to quartz above 870°, whereas the reverse is true; it is probably safe therefore to say that quartz is unstable with respect to cristobalite above this temperature. As the liquid phase provides a fluid medium in which molecular rearrangement can easily operate, it is likely that the more fluid the liquid and the greater the amount of liquid the more rapid will be the catalysis. This statement appears to be in line with the facts.

TABLE XIV

TEMPERATURE INITIATING α–β CRISTOBALITE INVERSION SHOWN BY SUDDEN THERMAL EXPANSION

Sample (%)	Firing treatment (hr.)	Firing treatment (°C.)	Density	Initial temp. (°C.)
Quartz + 0.1 Na_2MoO_4	4	1450	2.30	220
" " 0.1 CaO	4	1450	2.33	230
" " 2.0 Na_2HPO_4	2	1450	2.31	230
" " 0.5 KOH	2	1500	2.31	235
" " 1.0 NaF	2	1300	2.31	237
" " 2.0 Li_2CO_3	2	1450	2.31	246
" " 2.0 Na_2CO_3	2	1450	2.32	248
" " 2.0 K_2CO_3	2	1450	2.30	250
" " 2.0 LiCl	2	1450	2.32	251
" " 0.5 NaOH	2	1500	2.31	253

(2) Solid Phase Reaction

Some evidence has been gathered which indicates that, at least in the case of the alkali carbonates or hydroxides, the quartz inversion can be catalyzed in the absence of a liquid. A possible mechanism for this is (1) $Na_2CO_3 \rightarrow Na_2O + CO_2$; (2) Na_2O + quartz $\rightarrow Na_2SiO_3$; (3) $Na_2SiO_3 \rightarrow Na_2O$ + cristobalite; (4) Na_2SiO_3 + cristobalite $\rightarrow Na_2Si_2O_5$; and (5) $Na_2Si_2O_5 \rightarrow Na_2O$ + 2 tridymite. By a repetition of steps (2), (3), (4), and (5), the cycle in that order can continue until all of the quartz is used. It is not known whether Na_2SiO_3 and $Na_2Si_2O_5$ are really the intermediate phases, but they are at least probable. The greater activity of the alkali compounds as contrasted with other substances is ascribed to their relatively greater ease of dissociation on heating so that the free alkali oxide becomes available for such a cycle as that described. Acid oxides, such as B_2O_3, P_2O_5, and TiO_2, appear to be poor catalysts, if not actually inhibitors of the quartz-cristobalite inversion.

The same catalysts which function best in the change of quartz to cristobalite would also be the best for the reverse process. As this must be carried on below 870°C., however, the rates are too slow to be important except for refractories or other materials subjected to long-time heating at approximately 750° to 850°C.

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FUNDAMENTAL STUDY OF CLAY: PREPARATION OF A PURIFIED KAOLINITE SUSPENSION, I*

By A. L. Johnson and F. H. Norton

Abstract

A method of preparing clean clay suspensions is described. Organic matter is removed by hydrogen peroxide and sodium hydroxide digestion, followed by an electrodialysis treatment to remove other inorganic salts and to prepare a clay-water suspension. After NaOH is added, viscosity and titration values are given for (*a*) a regular water-washed Florida clay, (*b*) the same clay after electrodialysis, and (*c*) the same clay after a thorough cleaning according to the method described. If the sample contains lignite, a clean clay exhibits rheopexy at certain concentrations of NaOH.

I. Introduction

This paper, the first in a series giving the results of a study on the fundamental properties of kaolinite slips, describes the laboratory method developed to prepare clean kaolinite, $Al_2Si_2O_5(OH)_4$, from commercial clays.

Mineralogically, whiteware clays contain kaolinite as the principal constituent, but the lack of similarity in properties between different raw clays is annoying, and reasons for these differences are needed. Before a comparison of the properties of clays can be made successfully, the condition of the raw material must be defined. A chemical analysis, until recently, has been widely used to account for differences in the behavior of samples caused by variations in their chemical composition. The shortcomings of this technique are now recognized, and other methods of analysis are being developed slowly with promise of greater success. Clays and other ceramic materials, because of their fine grain size, are a problem for the colloid chemist, and a combination of colloidal and physicochemical methods should therefore be utilized in an effort to give a complete definition and to analyze the condition of a raw clay.

(1) Review of Investigations

Henry and Taylor[1] show certain rough similarity of results in base-exchange capacity and viscosity on four electrodialyzed commercial clays. Speil,[2] working with electrodialyzed monodisperse fractions of Florida clay, shows the effect of size distribution on total surface area. He points out that a linear relation exists between surface area and certain properties such as base-exchange capacity, plasticity, and dry strength. Whittaker[3] states that the plasticity of kaolinite is directly related to surface area and inversely related to particle size. Harman and Fraulini[4] show that base exchange is proportional to surface area only in the smaller sizes.

On the basis of these studies and other work, an explanation for the variation in properties between kaolinite clays may be found because of differences between samples in (*a*) particle shape, (*b*) particle-size distribution and its effect on the total surface area, (*c*) adsorbed ions, (*d*) traces of other associated materials of an organic or an inorganic nature, and (*e*) adsorbed gases.

If these variables are controlled and properly adjusted on samples of kaolinite heretofore differing in properties, a stabilization of properties peculiar to the specific conditions prevailing at the time of the tests would possibly occur. The effect then of any one variable could be easily studied.

(2) Suggested Methods

Two modes of attack are possible in the evaluation of samples of ceramic materials. The first method consists of a determination of the amount and type of impurity existing in the sample. Rapid strides have been made in the detection of small quantities of impurities in clays by the use of X rays,[5] by differential thermal analysis,[6] and by the determination of exchangeable bases.[7] Although these tests afford a means for the evaluation of the sample, the complexity of the study is increased because the effects of such impurities in clays have not been determined directly.

The second method consists of stripping the clay of all its impurities regardless of their identification, and the writers present a detailed description of this method.

II. Removal of Organic Matter

Robinson[8] has given a laboratory method for the removal of lignite by hydrogen peroxide; the method is

* Received September 9, 1940.

[1] E. C. Henry and N. W. Taylor, "Acid and Base Binding Capacities and Viscosity Relations in Certain Whiteware Clays," *Jour. Amer. Ceram. Soc.*, **21** [5] 165–75 (1938).

[2] S. Speil, "Effect of Adsorbed Electrolytes on Properties of Monodisperse Clay-Water Systems," *ibid.*, **23** [2] 33–38 (1940).

[3] H. Whittaker, "Effect of Particle Size on Plasticity of Kaolinite," *ibid.*, **22** [1] 16–23 (1939).

[4] C. G. Harman and Felix Fraulini, "Properties of Kaolinite as Function of Its Particle Size," *ibid.*, **23** [9] 252–59 (1940).

[5] R. E. Grim and R. H. Bray, "Mineral Constitution of Ceramic Clays," *ibid.*, **19** [11] 307–15 (1936).

[6] F. H. Norton, "Critical Study of Differential Thermal Method for Identification of Clay Minerals," *ibid.*, **22** [2] 54–63 (1939).

[7] (*a*) S. E. Mattson, "Electrodialysis of Colloidal Soil Material and Exchangeable Bases," *Jour. Agr. Research*, **33**, 553–67 (1926).

(*b*) R. P. Graham and J. D. Sullivan, "Critical Study of Methods of Determining Exchangeable Bases in Clays," *Jour. Amer. Ceram. Soc.*, **21** [5] 176–83 (1938).

[8] W. O. Robinson, "Determination of Organic Matter in Soils by Means of Hydrogen Peroxide," *Jour. Agr. Research*, **34** [4] 339–56 (1927).

convenient because there is no apparent action on the kaolinite particles. A sample of clay is blunged in distilled water and screened through a 325-mesh screen to remove the larger particles of lignite and to expedite their removal with H_2O_2. About 1% of 30% H_2O_2 (based on the clay weight) is added to the slip, and the reaction proceeds at room temperature with frequent agitation over a period of several days. When the reaction has somewhat subsided, another portion of H_2O_2 is added and is agitated frequently as before. This procedure is repeated until the evolution of gases has ceased. The bulk of the lignite is decomposed by the peroxide in the form of CO_2. The presence of soluble organic compounds as by-products, however, is also indicated, and these must be removed by washing with large volumes of distilled water made slightly alkaline with NaOH. If the amount of NaOH added is not excessive, the clay will settle and the supernatant liquid can be drawn off. For the clays thus treated, NaOH additions with a pH of from 5.0 to 6.2 are possible, and the clay will settle under the influence of gravity in a number of hours. The passage of this dilute slip through a centrifuge to remove the water will facilitate this process, but from three to five NaOH washes will be necessary. As a precautionary measure, the hydrogen peroxide treatment may be repeated at this point to remove any remaining lignite. Two or even three such treatments are advisable for ball clays which have a high content of organic matter.

III. Removal of Inorganic Salts

The method for the removal of inorganic salts from aqueous solution by an electrodialysis operation has been used by research workers as a rapid and usually effective tool. The presence of clay in this solution may complicate the procedure because clay has a great affinity for certain ions. Mattson[7(a)] states that only the ionized portion of the compound is removed. The hypothetical combination of a weakly ionized salt, held strongly to the clay particle, consequently would involve the expenditure of considerable work and time before the process of electrodialysis could entirely remove such an impurity from the clay.

For this reason, preliminary studies were made on this process, and some of the more important results will be discussed.

(1) Electrodialysis Process

The electrodialysis operation is carried out in a three-compartment Mattson cell with a capacity of from 1 to 1.5 liters of solution. The end cells are made of porcelain, and the center compartment is made of Haveg, a commercial plastic material.* The compartments are separated by membranes, and they are held together with two clamps which make the cell watertight. The same results may be obtained by the use of vegetable parchment paper or dialysis cellophane for membranes. The anode is a graphite sheet, and the cathode is copper. Provision is made for the use of 110- or 220-volt d. c., as the need arises. The voltage at the beginning of a run is usually 110, but after the bulk of the ions has been removed, 220 volts may be used without danger of overheating from excessive current. Distilled water is circulated continuously in the end cells throughout the operation. The clay may tend to migrate toward the anode during electrodialysis, and a rubber V-shaped stirrer is provided to scrape the material from the parchment. This stirrer also keeps the clay in suspension and increases the rate of electrodialysis.

After the clay has been treated to remove the lignite, leached with NaOH, and washed with water, about 1½ liters of a 10 to 20% suspension are placed in the center compartment of the cell for electrodialysis. A record is kept of the time, volts, amperes, temperature, and pH of the suspension to determine the end point of the process.

Figure 1 shows the type of data obtained by the electrodialysis treatment on a Florida kaolin after the organic matter has been decomposed with hydrogen peroxide and the clay has been leached with NaOH and washed with water. The electrodialysis is said to be complete when no change occurs in the pH of the suspension or in current density with further electrodialysis. In this case, the pH of the suspension at the end point is 4.7, the current density at 30°C., 0.00011 ampere per sq. cm. (Fig. 1).

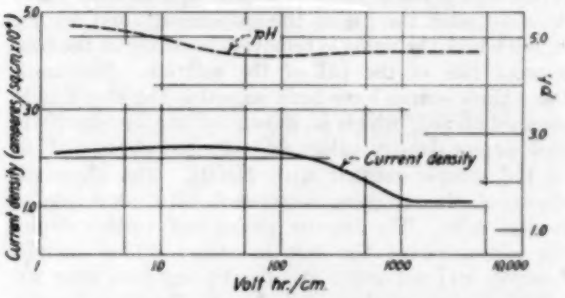

FIG. 1.—Current density at 30°C. and pH on electrodialyzing treated Florida clay.

As a precaution after this first electrodialysis, the clay is washed several times with distilled water and NaOH; finally an excess of NaOH is added, and the material is re-electrodialyzed. If the end point in the electrodialysis is similar to the previous data, the clay is said to be completely electrodialyzed. Sometimes three or four treatments with NaOH and re-electrodialyses are necessary before the end point becomes constant.

Because electrodialysis removes only the ionized portion of compounds, it follows that the greater the degree of ionization, the greater the speed of removal. Acid- or base-forming monovalent substances are more highly ionized than the di- or tri-valent elements or radicles. A longer period of time therefore would be required to remove such polyvalent salts by electrodialysis.

* Haveg may be obtained from the Haveg Corporation, Newark, Del.

Figure 2 shows the rate of electrodialysis on clean samples of kaolinite, one treated with NaOH and the other with potassium alum. The solid curve shows the current density at 30°C. vs. volt hours per centimeter, and the broken curve shows the pH value of the suspension during the stages of this treatment.

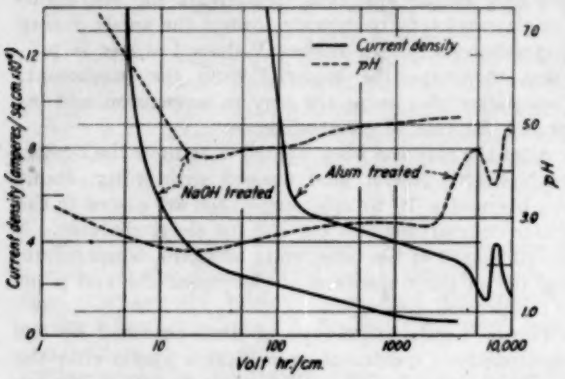

FIG. 2.—Electrodialysis data on clean samples of Florida clay treated with potassium alum and sodium hydroxide.

It will be noticed that salts are removed in definite steps as follows: (*a*) the region where the removal of the cation predominates, which lowers the pH of the suspension; (*b*) the region where the removal of both cation and anion is more or less in equilibrium, which does not alter the pH of the suspension; and (*c*) the region where the anion is removed, resulting in the consequent rise of the pH of the solution. Not until these three stages have been passed is the clay finally electrodialyzed, which is shown by the constant pH and current density values on prolonged electrodialysis of the sample treated with NaOH. The electrodialysis of the suspension treated with alum shows similar data. The regular peaks and valleys depict the ionization of the salt in stages. This sample, however, did not arrive at an end point even after 800 hours of electrodialysis, whereas in the clean sample treated with NaOH, electrodialysis is complete after from 40 to 80 hours, depending on the initial cleanliness of the material.

These and other tests show that all inorganic materials cannot be removed from clay by a mere "48 hours of electrodialysis." It is questionable in fact if certain salts of the polyvalent type can be removed by electrodialysis in any practical period of time. Electrodialysis therefore is not a "cure-all" in any sense of the word, and the actual condition of the sample after such treatment should not be taken for granted.

By a careful consideration of proper leaching agents, certain inorganic materials present in clays which are not readily removed by electrodialysis can be leached out with water after they are converted to the soluble form. The material used for the leaching operation can be easily removed by electrodialysis in a comparatively short time if it is a highly dissociated compound, such as NaOH or HCl.

Until it is known what properties the various inorganic materials impart to a kaolinite-water system, the type of salt in contact with the clay must be chosen carefully. The indiscriminate use of dispersants and flocculants in clay-washing operations for this reason may cause a great deal of harm. It has been necessary, therefore, to employ untreated clays for this study, as the removal of certain ions has been difficult, and small traces of these materials have a profound influence on the viscosity relations of this ceramic material.

A clay treated in the manner outlined should be thoroughly rid of impurities, such as soluble salts and organic material, and the miscellaneous adsorbed ions should be replaced with hydrogen and the hydroxyl group. In this state, fractions of the desired particle distribution from the purified clay can be readily prepared by the method of Norton and Speil.[9] Recent developments[10] on the refinement of clay by flotation aids the removal of the associated mineral impurities, such as quartz, mica, and feldspar. Grim and Bray,[5] however, show that certain minerals have a tendency to restrict themselves to definite size limits in the clays they studied, and therefore such impurities might automatically exclude themselves in the fractionation. The particle shape of the fractions prepared can then be checked by means of proper equipment, and adsorbed gases can be removed by suitable deairing devices. In this manner, all of the variables mentioned, which probably affect the properties of clay slips, may be evaluated and controlled.

IV. Properties of the Purified Kaolinite Suspension

Before the actual preparation of closely monodisperse fractions was started, it was necessary to study the material to determine the effect of the cleaning operation on the properties of the clay.

The importance of the viscosity relations of clay suspensions on additions of electrolytes as a test for comparison between samples need not be stressed. Other investigators, however, have failed thus far to correlate such data on individual clays with their behavior in the combination of clays and nonplastic material which constitute ceramic casting slips. One reason for this lack of correlation may be due to the fact that the test is extremely sensitive and not enough emphasis has been placed on the preparation of samples.

Various methods and numerous instruments are used to measure the viscosity of clay suspensions. Each particular type of viscosimeter is chosen because of its adaptability to the work on hand. After a study of the various instruments, the MacMichael viscosimeter[11] was selected for this work because of certain definite advantages. Several modifications were incorporated in the design and construction of the in-

[9] F. H. Norton and S. Speil, "Fractionation of a Clay into Closely Monodispersed Systems," *Jour. Amer. Ceram. Soc.*, **21** [10] 367–70 (1938).

[10] O. C. Ralston, "Flotation and Agglomerate Concentration of Nonmetallic Minerals," *U. S. Bur. Mines Repts. Investigations*, No. 3397, 63 pp.; *Ceram. Abs.*, **18** [2] 59 (1939).

[11] R. F. MacMichael, "Testing of Clay," *Trans. Amer. Ceram. Soc.*, **17**, 639–59 (1915); see also *Jour. Ind. Eng. Chem.*, **7**, 961–63 (1915).

strument (Fig. 3). The speed of the outer cup may be controlled continuously between 1.5 and 120 r.p.m. Damping magnets prevent undue oscillation, thereby giving the true reading in a shorter period of time. With critical damping, a direct reading of the yield points may be obtained on slips. This is not possible with the majority of viscosimeters.

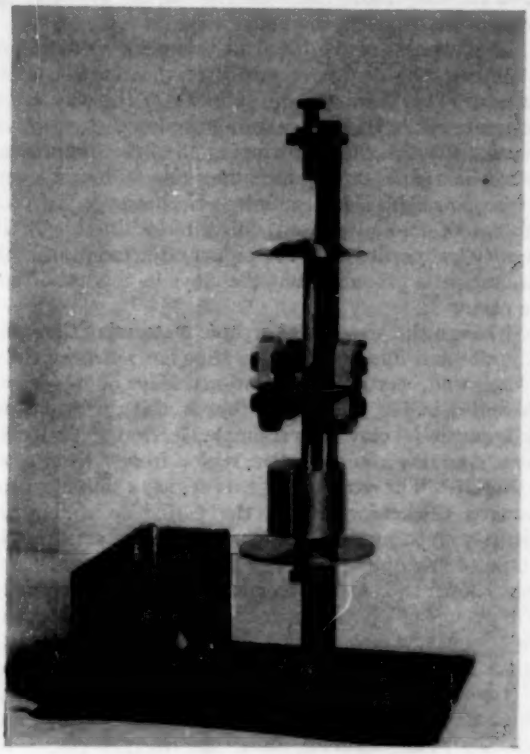

FIG. 3.—Modified MacMichael viscosimeter.

In the calibration of the instrument, any solution of known viscosity is placed in the cup of the viscosimeter and held at the required temperature. The angle of twist in degrees MacMichael is observed for one or two speeds. Sucrose solutions are convenient for this work, and standard data on them may be obtained from the International Critical Tables. For the heavier wires, standard oils may be used successfully in the same manner. This type of calibration gives the angle of rotation for any wire directly in viscosity units. In the range from 1 to 1500 centipoises, a precision of between 0.3 and 0.5% is possible.

Each wire can also be calibrated to give the shearing stress in fundamental units for any angular rotation. From the dimensions of this instrument, the rate of shear is obtained from the formula,

$$\text{Rate of shear} = 2.85 \times \text{r.p.s.}$$

The results on any sample studied may also be expressed in terms of rate of shear and shearing stress. These units are convenient in the study of the types of flow obtained in clay-water systems.

Figure 4 shows the results of viscosity determinations on samples of clay slips at 16% of solids by weight with increasing amounts of NaOH. The three curves represent data on the water-washed Florida clay (*a*) as received with no treatment; (*b*) after a simple electrodialysis treatment; and (*c*) after H_2O_2 digestion, NaOH leach, and a final electrodialysis operation. Figure 5 shows the titration results on these samples.

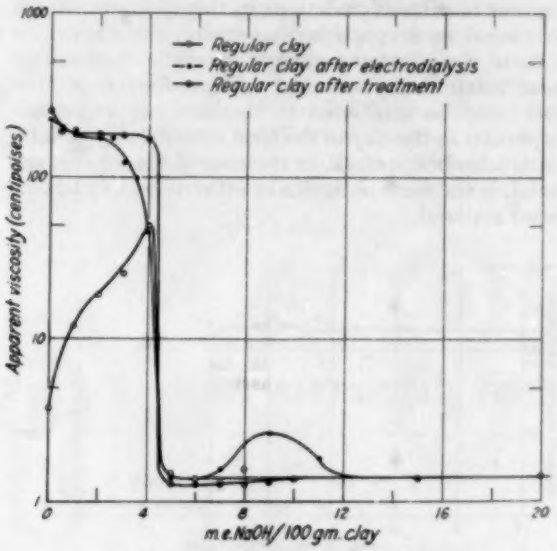

FIG. 4.—Viscosity relations of Florida clay at 16% solids by weight after various stages in cleaning treatment.

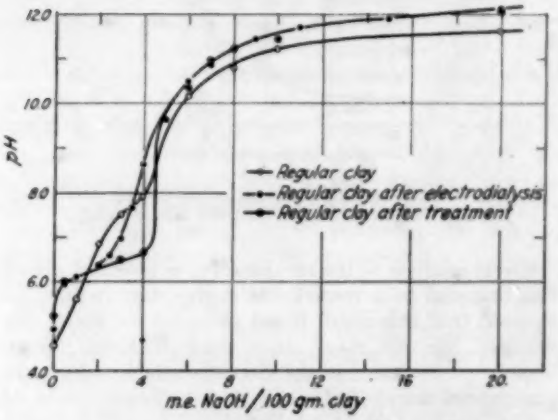

FIG. 5.—Titration relations of Florida clay in various stages of cleaning treatment.

The viscosity and titration results on the thoroughly cleaned clay after additions of HCl and NaOH are given in Figs. 6 and 7. The electrodialyzed clay is not allowed to dry because this seems to alter the properties somewhat. Just what occurs has not yet been determined, but precautions are taken not to dry this material in the electrodialyzed condition. The correct proportions of clay, water, and NaOH are placed in

glass-stoppered bottles, and two days are allowed for equilibrium to be established.

The curves in Figs. 4 and 5 show that different results are forthcoming, depending on the condition of the sample. This state of affairs has plagued the clay industry for some time because it has been difficult to give a complete definition of the system on which many reported observations have been made. The differences in viscosity relations in this case are not due to variations in particle shape, size distribution, or even to the associated mineral impurities because the same batch of clay was used. These differences, however, may be attributed to the inorganic or organic impurities in the clay in the form of soluble or insoluble salts, adsorbed ions, or, in the case of the organic material, in the form of lignite or other types of carbonaceous material.

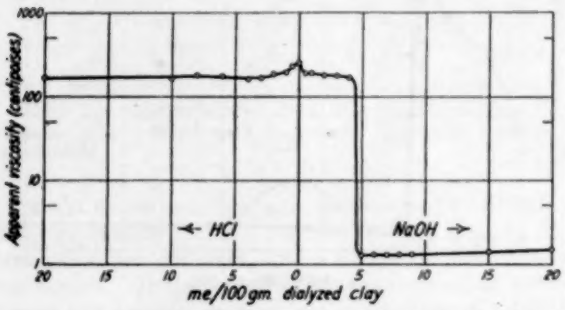

FIG. 6.—Viscosity relations of clean Florida clay at 16% solids (weight).

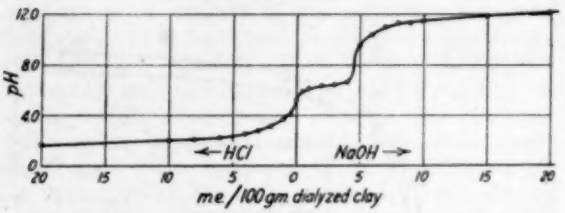

FIG. 7.—Titration relations on addition of HCl and NaOH to clean electrodialyzed Florida clay.

Electrodialysis of the regular clay, as received, cleans this material to a remarkable degree, but it must be stressed that this result is not obtained for every clay studied. Certain clays, after electrodialysis, showed little or no deviation in the viscosity relations from the commercial sample, indicating that the impurities could not be removed by electrodialysis alone.

The data in Figs. 6 and 7 show the complete picture of the viscosity and titration relations of the clean clay after additions of HCl and NaOH. The complete agreement between the viscosity and titration data is interesting. No appreciable change occurs in the viscosity relations on the acid side, indicating possibly that the clay in the electrodialyzed condition has no affinity for HCl. The titration curve is substantially the same as would be obtained if the pH of water were measured with progressively larger additions of HCl.

The data on the basic side show that the clay and NaOH enter into an ion exchange. Until at least 4 m.e. of NaOH per 100 gm. of electrodialyzed clay have been added, little change in the viscosity or titration results takes place. The action in this region is similar to the buffer action of certain weak acids and their salts. As soon as an excess of NaOH is added, the pH of the suspension rises quickly and the viscosity of the mixture drops as suddenly.

The sharpness of the break at this point would tend to indicate the degree of purity of the reacting substances. This points to the stability of the clay after the treatment. Because certain samples of these clays revealed the difficulty of stripping all of the impurities, certain inorganic or organic impurities still exist even in the so-called clean sample. If, however, several samples of kaolinite from different localities exhibit identical properties after the proper adjustment of each variable, it is probable that the clays in this condition are clean.

Although the presence of organic material in the form of lignite and its effect on clay slips has not been fully investigated, certain observations may be reported. The curve in Fig. 4, showing the viscosity relations on the commercial clay with a simple electrodialysis treatment, contains a hump in the region from 7 to 11 m.e. of NaOH. The samples in this region exhibit a pronounced thickening during the period in which the viscosity readings are taken. This phenomenon is a type of "rheopexy."[12] The thickening of the slip has been known to continue to increase even after from 10 to 15 hours of operation in the modified MacMichael viscosimeter, which is used for the study of viscosity on the samples. Henry and Taylor[1] observed a hump in viscosity on Georgia kaolin and Tennessee ball clay, which they attribute to the presence of some swelling mineral. This behavior, more than likely, is caused by the presence of humates or humic acid which result from the action of NaOH on lignite or other organic matter.

A simple test served to indicate that this is the cause of the phenomenon. A portion of the extract, obtained by digesting lignite with distilled water at about 70°C., was added to a sample of the clay which had been previously cleaned, but the test revealed no hump in the viscosity curve. Sodium hydroxide was added to the required concentration, and the samples were allowed to stand for two days, with no agitation during the last 24 hours. The viscosity results of this slip showed the hump in the region of from 7 to 16 m.e. of NaOH, with the maxima in the vicinity of 10 m.e. This sample was then treated with H_2O_2, washed with NaOH, electrodialyzed, and retested, whereupon this characteristic disappeared.

The presence of a minute quantity of lignite thus is shown to affect profoundly the viscosity of a dilute slip

[12] H. Freundlich and F. Juliusburger, "Thixotropy, Influenced by Orientation of Anisotropic Particles," *Trans. Faraday Soc.*, **31**, 920–21 (1935). Note: According to Freundlich's definition, the phenomenon observed in this work is not strictly rheopexy, but this term more accurately defines the phenomenon than any other.

of kaolinite and water. Just what the effect would be at higher concentrations and with other types of organic material is not yet known. The point to be stressed is that a change in the viscosity results when lignite and NaOH are added to the clay which would not be present with NaOH additions alone. Many other types of data obviously could be obtained if a study of the effect of various inorganic salts were made; this, however, is beyond the scope of the present paper.

V. Conclusions and Future Work

It is not possible to state definitely on the basis of this work whether, by stripping a clay of inorganic salts, organic matter, and adsorbed ions and by controlling its particle-size distribution, a stabilization of the properties of this ceramic material will result. If, however, samples of whiteware clays from widely scattered areas do exhibit identical properties after analysis and treatment in preparing carefully fractionated systems, then there is a great probability that such treatment has produced pure kaolinite. Tests on this clay will give fundamental information on this essential industrial material and serve as a basis for future studies.

Work has already been started on the preparation of closely monodisperse fractions from several whiteware clays in an effort to check the properties one with the other, and this work will be reported.

Progress is also being made on the determination of the effect of certain commercial deflocculants on the dispersion of clean clay. This phase of the work should add information on the application of the mechanism of dispersion to ceramic casting slips.

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THERMAL AND MOISTURE EXPANSION OF KAOLINS AND BODIES FIRED TO DIFFERENT TEMPERATURES*

By H. Thiemecke

Abstract

Thermal-expansion and moisture-expansion determinations were made on four kaolins of the Georgia, Florida, North Carolina, and English types alone and on typical semivitreous, hotel china, and electrical porcelain bodies embodying each of these kaolins after being fired at cones 6, 9, and 11. The Georgia and Florida kaolins and bodies showed surprisingly similar expansion characteristics. The general order of decreasing thermal expansion and increasing moisture expansion of the kaolins at all three firing treatments was Georgia, Florida, North Carolina, and English china. The semivitreous bodies at cones 6 and 9 showed the same order of expansion as the kaolins alone, but at cone 11 the thermal expansion of the English china clay body was the highest and the North Carolina kaolin body next in order. Moisture expansion of the bodies at cone 11 was found to be a function of the absorption, regardless of the kaolin used with no expansion obtaining at zero absorption. Mixtures of clay, flint, and feldspar, given an autoclave treatment after being fired to cones 6 and 9, showed that feldspar additions increased moisture expansion. When these mixtures were dehydrated at different temperatures, the data obtained were insufficient to confirm any theory on the nature of moisture expansion in a porous ceramic body.

Part I

I. Introduction

Previous investigators[1] have shown that differential thermal and moisture expansions between the body and glaze are important factors in the service performance of ceramic glazed ware when they are subjected to temperature changes and to exposure under varying moisture conditions.

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* Thesis presented for the Professional Degree of Ceramic Engineer, Ohio State University, Columbus, Ohio, 1940. Received June 24, 1940.

[1] (*a*) Herman Harkort, "Method of Testing Crazing of Whiteware," *Trans. Amer. Ceram. Soc.*, **15**, 368–72 (1913).

(*b*) G. E. Merritt and C. G. Peters, "Interferometer Measurements of Thermal Dilatation of Glazed Ware," *Jour. Amer. Ceram. Soc.*, 9 [6] 327–42 (1926).

(*c*) H. G. Schurecht, "Methods for Testing Crazing of Glazes Caused by Increases in Size of Ceramic Bodies," *ibid.*, **11** [5] 271–77 (1928).

(*d*) H. G. Schurecht and G. R. Pole, "Effect of Water in Expanding Ceramic Bodies of Different Compositions," *ibid.*, **12** [9] 596–604 (1929).

(*e*) H. G. Schurecht and G. R. Pole, "Method of Measuring Strains Between Glazes and Ceramic Bodies," *ibid.*, **13** [6] 369–75 (1930).

(*f*) E. P. Wright, "Study of Absorption of Two Earthenware Bodies and Their Resistance to Crazing in Steam Test," *ibid.*, 12 [2] 118–22 (1929).

(*g*) R. G. Mills, "Use of Autoclave in Testing Ceramic Products for Resistance to Crazing," *ibid.*, **13** [12] 903–14 (1930).

(*h*) R. C. Purdy, "Coefficient of Expansion of Porcelain

Whether or not the moisture expansion of a glaze is variable,[2†] its thermal expansion can be modified within limits by changes in composition.[3] Modifications of thermal and moisture expansion in a body can be also effected by composition changes, but such changes are limited by the required physical working properties in the unfired state. Where kaolins represent only part of the plastic content of a body and if they effect dissimilar thermal and moisture expansions in the fired body without appreciably affecting other physical properties, a replacement of one or more to gain the desired end suggests itself.

II. Materials

Thermal- and moisture-expansion data were obtained on four kaolins, namely, Pioneer Georgia, EPK Florida, Kamec North Carolina, and No. 1 English china clay fired at three different temperatures, and also on four groups of typical bodies in which each body of a group contained but one of the four kaolins.

Bodies Nos. 65 and 95 were made to determine whether the thermal- and moisture-expansion properties were additive when kaolins were jointly incorporated in a body.

III. Preparation of Specimens

The plastic kaolins and bodies were extruded into $^3/_8$-in. diameter rods, dried and fired in tunnel kilns as follows: kaolins to cones 6, 9, and 11; group I to cone 6; group II to cone 9; and groups III and IV to cone 11. Test pieces, 154 mm. long, were cut from the rods for thermal-expansion determination, and a groove was ground in each piece to accommodate the thermocouple. The rods for the moisture-expansion measurements were cut approximately 203 mm. long, and the ends were ground to a small diameter so as to approach single-point contact when expansions were determined with the micrometer.

TABLE I

COMPOSITIONS OF BODIES

Group I, cone 6 semivitreous

	Body No. 61 (%)	62 (%)	63 (%)	64 (%)	65 (%)
Bell's dark ball clay	16	16	16	16	16
Bell's Dresden ball clay	16	16	16	16	16
Flint	25	25	25	25	25
Loomis talc	6	6	6	6	6
N. C. pyrophyllite	8	8	8	8	8
N. C. feldspar	9	9	9	9	9
Ga. kaolin	20				5
Fla. kaolin		20			5
N. C. kaolin			20		5
English china clay				20	5

Group II, cone 9 semivitreous

	Body No. 91 (%)	92 (%)	93 (%)	94 (%)	95 (%)
No. 4 Ky. ball clay	16	16	16	16	16
Bell's dark ball clay	15	15	15	15	15
Flint	36	36	36	36	36
N. C. feldspar	12	12	12	12	12
Ga. kaolin	21				5.25
Fla. kaolin		21			5.25
N. C. kaolin			21		5.25
English china clay				21	5.25

Group III, cone 11 electrical porcelain

	Body No. 111 (%)	112 (%)	113 (%)	114 (%)
Bell's Dresden ball clay	15	15	15	15
No. 4 Ky. ball clay	15	15	15	15
N. C. feldspar	30	30	30	30
Flint	20	20	20	20
Ga. kaolin	20			
Fla. kaolin		20		
N. C. kaolin			20	
English china clay				20

Group IV, cone 11 hotel china

	Body No. 115 (%)	116 (%)	117 (%)	118 (%)
No. 4 Ky. ball clay	9	9	9	9
Dolomite	1.5	1.5	1.5	1.5
S. Dak. feldspar	17	17	17	17
Flint	36.5	36.5	36.5	36.5
Ga. kaolin	36			
Fla. kaolin		36		
N. C. kaolin			36	
English china clay				36

IV. Methods of Testing

(1) Thermal Expansion

Thermal-expansivity measurements were made from atmospheric temperatures of 25° to 625°C. with a dilatometer similar to that used by Sievert and Moffat.[4]

To insure heat distribution in the test piece, a brass tube liner was floated inside the refractory tube of the combustion furnace. The frame, which supported the nonmoving quartz glass rod and the Ames dial gauge,

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Body Mixtures," *Trans. Amer. Ceram. Soc.*, **15**, 499–522 (1913).

(*i*) H. H. Holscher, "Expansion of Ceramic Bodies Caused by Liquid and Vapor Penetration," *Ohio State Univ. Eng. Expt. Sta. Circ.*, No. 22, 24 pp. (1931); *Ceram. Abs.*, **16** [2] 68 (1937).

(*j*) R. F. Geller and A. S. Creamer, " 'Moisture Expansion' of Ceramic Whiteware," *Bur. Stand. Jour. Research*, **9** [3] 291–307 (1932); R.P. 472; *Ceram. Abs.*, **11** [12] 622 (1932).

(*k*) E. H. Lintz, "Use of Talc and Pyrophyllite in Semivitreous Dinnerware Bodies," *Jour. Amer. Ceram. Soc.*, **21** [6] 229–37 (1938).

[2] (*a*) H. G. Schurecht and G. R. Pole, "Moisture Expansion of Glazes and Other Ceramic Finishes," *ibid.*, **14** [4] 313–18 (1931).

(*b*) L. H. Milligan and David Armitage, " 'Moisture Expansion' of Glasses," *ibid.*, **15** [3] 167–70 (1932).

† In a recent unpublished investigation, the author found that a cone 5 glaze, with the molecular formula of

$$\left.\begin{matrix}0.208\ KNaO\\0.490\ CaO\\0.302\ PbO\end{matrix}\right\}\ 0.301\ Al_2O_3\ \left\{\begin{matrix}3.00\ SiO_2\\0.354\ B_2O_3\end{matrix}\right.$$

showed no moisture expansion after it was melted, drawn into rods, and autoclaved over water at 100-lb. pressure for 3 hours.

[3] William Funk, Rohstoffe der Feinkeramik, p. 265. Julius Springer, Berlin, 1933; *Ceram. Abs.*, **13** [4] 103 (1934).

[4] G. E. Sievert and J. Moffat, Jr., "Expansion Strains in Initial Firing of Ceramic Ware," *Jour. Amer. Ceram. Soc.*, **23** [4] 122–24 (1940).

was made of pipe through which water was circulated. This eliminated radiation effects from the furnace.

The temperature of the test piece was increased 150°C. per hour. This rate gave sufficiently uniform heat distribution throughout the specimen as indicated by the expansions at the silica inversion temperatures.

(2) Moisture Expansion

Moisture-expansion measurements were made with a micrometer graduated to read to hundredths of a millimeter. Because atmospheric moisture was sufficient in some bodies to cause an expansion of 0.02%, the fired rods were cut to proper length, heated again to approximately 700°C. through a decorating kiln, and cooled in a desiccator over sulfuric acid. They were then measured, autoclaved over water at 100 lb. of pressure for 3 hours, and immediately remeasured.

To determine whether the moisture expansion was reversible by dehydration, the autoclaved rods were held at 150°C. for 24 hours, fired through a decorating kiln, and then fired to cone 08. The rods were cooled in a desiccator, and measurements were made after each heat treatment.

Shrinkage determinations were supplemented on a number of specimens with weight-loss measurements, but it was found that after the decorating kiln treatment the weight of the test pieces was less than that before autoclaving, indicating vaporization of the materials. In no case did any of the specimens regain the original weight when they were heated only to 150°C.

Absorption determinations were made on all of the specimens, following the procedure outlined by The American Ceramic Society Committee on Standards.[5] These values are shown Table II

TABLE II

PERCENTAGE ABSORPTION OF KAOLINS AND BODIES FIRED AT DIFFERENT TEMPERATURES

Body	Cone 6	Cone 9	Cone 11
Georgia kaolin	21.1	13.6	13.3
Florida kaolin	16.8	12.2	10.6
N. C. kaolin	27.9	24.7	24.4
English china clay	26.2	18.9	11.0
61	9.8		
62	10.2		
63	9.9		
64	6.7		
65	9.4		
91		8.5	
92		8.8	
93		8.8	
94		6.6	
95		8.4	
111			0.0
112			0.0
113			0.0
114			0.0
115			0.7
116			1.2
117			0.8
118			0.0

[5] "Standard Method for Behavior in Firing," *Jour. Amer. Ceram. Soc.*, **11** [6] 455 (1928).

V. Results and Discussion

(1) Thermal Expansion

Values for the linear thermal expansion of the kaolins and of the bodies are shown in Figs. 1 to 9, inclusive. The expansions were similar at all three firings for Georgia and Florida kaolins and for the bodies incorporating these kaolins. This would tend to bear out the contention of a number of geologists that the origin of these kaolins is the same.

The expansions for all four kaolins fired to cone 6 did not differ greatly. Similarly the cone 6 bodies, incorporating the kaolins alone, showed the same order of expansion. Fired to cone 9, the total thermal expansion of all of the clays, except the English china clay, increased. The expansions of the Georgia and Florida kaolins, fired to cone 9, showed a marked increase, particularly in the 100° to 200°C. range owing to the formation of cristobalite. These data agree with those obtained by Heindl, Pendergast, and Mong[6] and by McVay and Thompson.[7] Again, as at cone 6, the bodies incorporating the individual kaolins showed the same order of expansion as the kaolins.

When the firing was increased to cone 11, the expansions of the Georgia, Florida, and English china clays increased but slightly over that at cone 9. The North Carolina kaolin, however, showed a marked increase, although this was not evidenced in the North Carolina kaolin studied by Heindl, Pendergast, and Mong.[6]

The total expansion of the North Carolina kaolin and of the English china clay at cone 11 was less than that of the Georgia and Florida kaolins. The order of expansion, however, of the fired bodies containing these clays was reversed, the English china clay body having the greatest expansion and the North Carolina kaolin body next in order. Fritz and Harrison[8] report similar results in tests on electrical porcelain bodies.

Because cristobalite has a higher coefficient of expansion than quartz[9] over the temperature range used in this investigation, it is questioned whether the greater expansion of the English china clay and North Carolina kaolin bodies is caused by the increased amount of cristobalite formed due to the greater flux content of these bodies contributed by the kaolins. Judging only from the expansion curves of the kaolins, the North Carolina kaolin and English china clay appear to develop less cristobalite per se than do the Georgia and Florida kaolins. If the increased expan-

[6] R. A. Heindl, W. L. Pendergast, and L. E. Mong, "Kaolins: Effect of Firing Temperature on Some of Their Physical Properties," *Bur. Stand. Jour. Research*, **8** [2] 199–215 (1932); R.P. 410; *Ceram. Abs.*, **11** [6] 387 (1932); also *Jour. Amer. Ceram. Soc.*, **16** [1] 75–76 (1933).

[7] T. N. McVay and C. L. Thompson, "X-Ray Investigation of Effect of Heat on China Clays," *Jour. Amer. Ceram. Soc.*, **11** [11] 829–41 (1928).

[8] E. H. Fritz and H. C. Harrison, "Symposium on 'Importance of Thermal History': III, Effect of Thermal History on Physical Properties of Electrical Porcelain," *Bull. Amer. Ceram. Soc.*, **18** [11] 420–21 (1939).

[9] R. B. Sosman, Properties of Silica, p. 363. American Chemical Society Monograph Series, No. 37, Chemical Catalog Co., Inc., New York, N. Y., 1927; *Ceram. Abs.*, **7** [7] 505 (1928).

sion of the North Carolina kaolin and English china clay bodies is due to increased development of cristobalite, other components of the bodies must have contributed to it or aided in its development in these kaolins.

(2) Moisture Expansion

The percentages of linear-expansion data, after autoclaving and dehydrating the kaolins and bodies at various temperatures, are given in Table III. As in the thermal-expansion studies, the kaolins fall into three classes, the Georgia and Florida kaolins exhibiting almost identical performances both alone and when they were incorporated in bodies.

At all three firings, the kaolins showed the same increasing order of moisture expansion after autoclaving, namely, Georgia, Florida, North Carolina, and English china clay, respectively. The same order also prevailed for the semivitreous bodies incorporating the individual kaolins at cones 6 and 9; in the cone 11 bodies, however, the moisture expansion appeared to be a function of approach to vitrification. No moisture expansion resulted in bodies of zero absorption, whereas in the hotel dinnerware bodies having slight absorption, the moisture expansion increased with the absorption regardless of the kaolin used. As found in the thermal-expansion studies, the composite kaolin bodies, fired at cones 6 and 9, showed additive moisture-expansion values for the kaolins.

When the rods were dehydrated at various temperatures (after autoclaving), it was found that, held at 150°C. for 24 hours, the kaolin rods approached their

TABLE III

PERCENTAGE OF MOISTURE EXPANSION OF KAOLINS AND BODIES FIRED AT DIFFERENT TEMPERATURES AFTER AUTOCLAVING AND DEHYDRATING AT DIFFERENT TEMPERATURES

Body No.	Cone No.	After autoclave (%)	Dehydrating treatment 150°C. (%)	700°C. (%)	Cone 08 (%)
Ga. kaolin	6	0.044	0.020	0.00	
	9	0.012	0.00		
	11	0.00			
Fla. kaolin	6	0.042	0.020	0.00	
	9	0.015	0.006	0.00	
	11	0.00			
N. C. kaolin	6	0.062	0.032	0.00	
	9	0.025	0.007	0.00	
	11	0.012	0.00		
English china clay	6	0.089	0.039	0.00	
	9	0.079	0.020	0.00	
	11	0.074	0.015	0.00	
61	6	0.074	0.045	0.016	0.00
62	6	0.072	0.042	0.012	0.00
63	6	0.078	0.054	0.020	0.00
64	6	0.084	0.054	0.020	0.00
65	6	0.076	0.052	0.020	0.00
91	9	0.110	0.064	0.025	0.020
92	9	0.108	0.059	0.025	0.015
93	9	0.115	0.069	0.028	0.022
94	9	0.121	0.073	0.030	0.023
95	9	0.113	0.069	0.025	0.020
111, 112, 113, 114	11	0.00			
115	11	0.016	0.010	0.010	0.00
116	11	0.021	0.015	0.013	0.00
117	11	0.020	0.015	0.015	0.00
118	11	0.00			

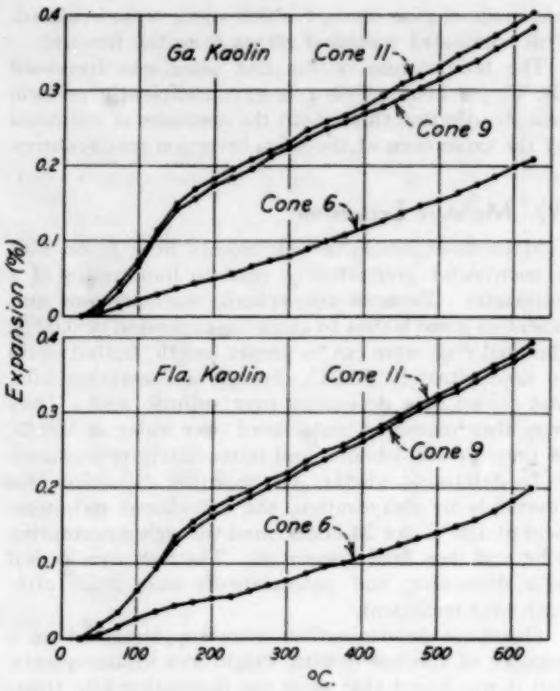

FIG. 1.—Thermal-expansion curves of one group of kaolins after firing at several different temperatures.

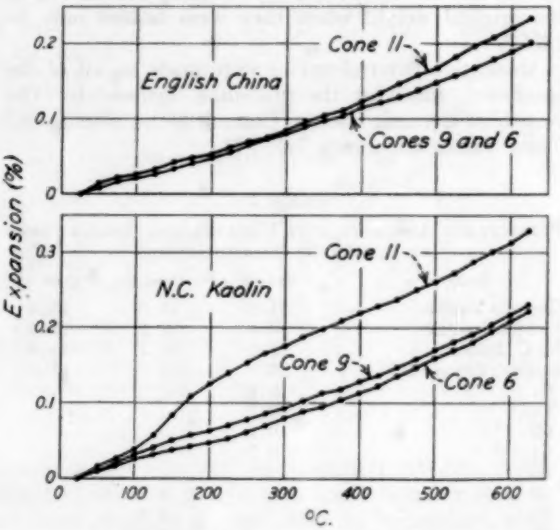

FIG. 2.—Thermal-expansion curves of two differing type kaolins after firing at several different temperatures.

original length more closely than did the bodies. At 700°C., the kaolins, regardless of firing, returned to their original lengths. This, however, was not true for the fired bodies, for only when they were heated to cone 08 did the majority return to zero expansion.

It is interesting to note that those that did not completely contract were the cone 9 semivitreous bodies containing a high percentage of flint.

One explanation for this might be that, with such a high flint component acting as an aggregate of anisotropic units, the unoriented particles, after reheating and cooling, expand unequally along different axes and leave small voids in the rods. A permanent expansion will therefore result even though all hydration has been eliminated. This condition would not exist if all of the particles were oriented in like manner and it would probably be even less likely with a decreased amount of aggregate. Another explanation might be that the moisture expansion occurring in kaolins alone is of a different character than that in bodies where other components are present.

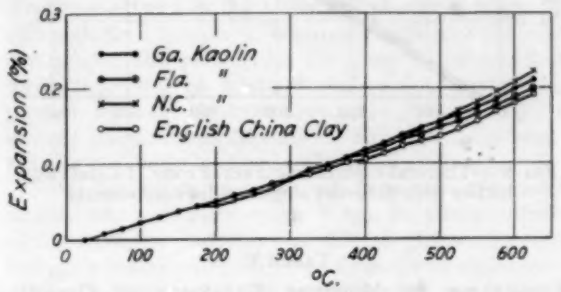

FIG. 3.—Thermal-expansion curves of four kaolins after firing at cone 6.

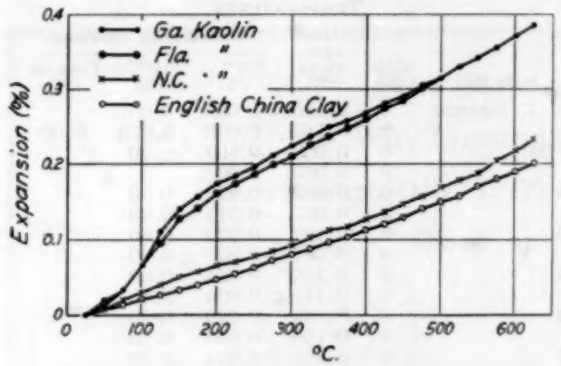

FIG. 4.—Thermal-expansion curves of four kaolins after firing at cone 9.

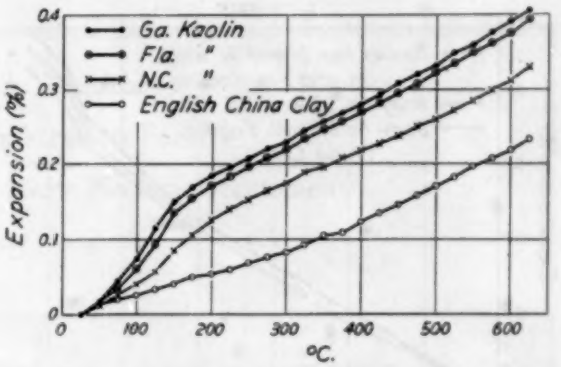

FIG. 5.—Thermal-expansion curves of four kaolins after firing at cone 11.

Part II

I. Moisture Expansion

A further attempt was made to ascertain the nature of the moisture expansion and to determine which component or combination of components in a normal whiteware body contributed most in this action. Three series of mixtures were made with Georgia kaolin, flint, and feldspar as end members, covering the ratios of these components normally found in various types of commercial bodies. The mixtures were fired to cones 6 and 9, autoclaved, and dehydrated as described in Part I. Rods of the nonplastic mixtures were made by mixing with a solution of polyvinyl alcohol to slip form and casting in plaster molds which were lined with tissue paper.

The compositions and absorptions are given in Table III.

TABLE IV

KAOLIN-FELDSPAR SERIES

	Body No.								
	1	2	3	4	5	6	7		
Ga. kaolin	58	56	54	52	50	48	46	64	0
N. C. feldspar	6	8	10	12	14	16	18	0	64
Absorption (cone 6)	14.6	13.6	12.6	11.7	10.9	10.2	9.4	21.1	16.8
Absorption (cone 9)	12.8	11.5	11.3	10.2	8.4	8.1	7.3	13.6	0.0

KAOLIN-FLINT SERIES

	Body No.					
	9	10	11	12	13	
Ga. kaolin	62	57	52	47	42	0
Flint	25	30	35	40	45	87
Absorption (cone 6)	23.0	23.4	23.6	23.7	23.7	26.6
Absorption (cone 9)	19.7	21.7	21.9	22.0	22.4	26.0

FELDSPAR-FLINT SERIES

	Body No.			
	14	15	16	17
N. C. feldspar	6	12	18	24
Flint	36	36	36	36
Absorption (cone 6)	28.8	28.7	28.7	28.8
Absorption (cone 9)	27.2	22.2	17.4	14.2

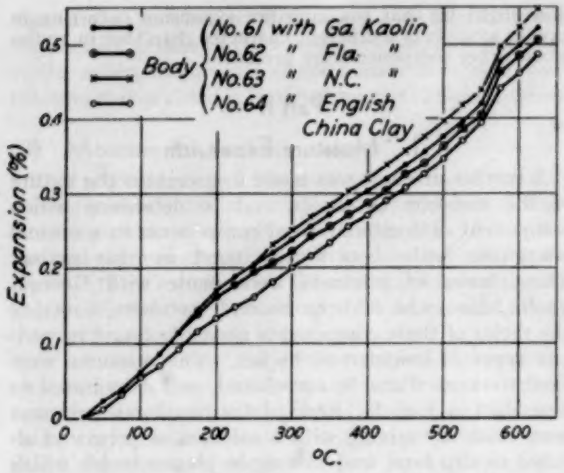

FIG. 6.—Thermal-expansion curves of cone 6 semi-vitreous bodies with different single kaolin components.

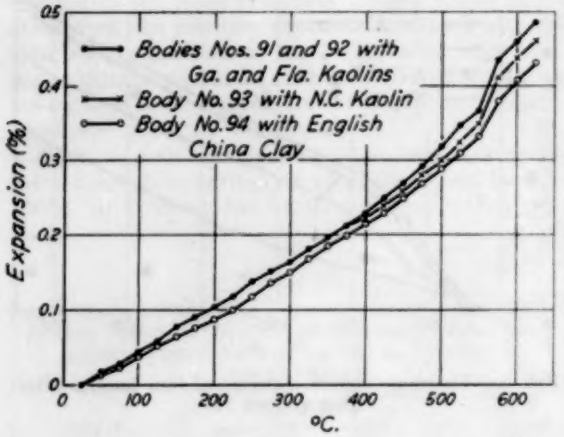

FIG. 7.—Thermal-expansion curves of cone 9 semi-vitreous dinnerware bodies with different single kaolin components.

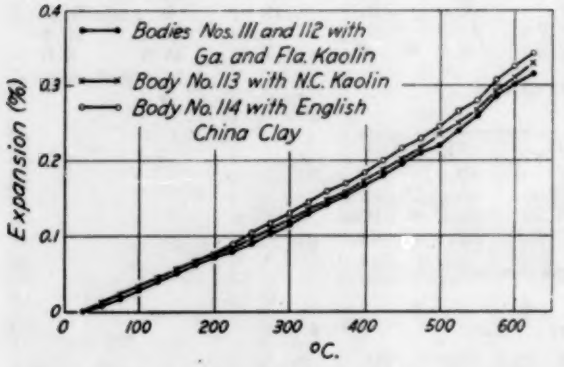

FIG. 8.—Thermal-expansion curves of cone 11 electrical porcelain bodies with different single kaolin components.

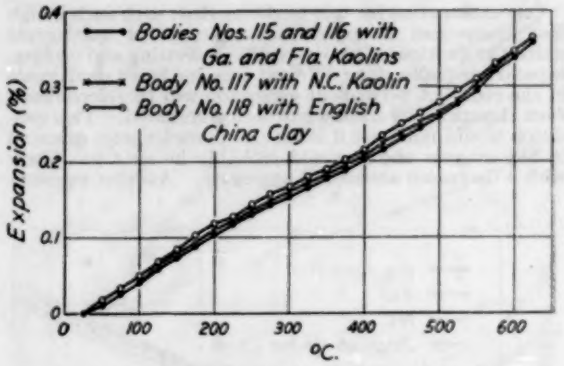

FIG. 9.—Thermal-expansion curves of cone 11 hotel china bodies with different single kaolin components.

TABLE V

PERCENTAGE OF MOISTURE EXPANSION OF GEORGIA KAOLIN, FLINT, AND FELDSPAR BODIES FIRED AT DIFFERENT TEMPERATURES AFTER AUTOCLAVING AND DEHYDRATING AT DIFFERENT TEMPERATURES

Body No.	Cone No.	After autoclave (%)	Dehydrating treatment 150°C. (%)	700°C. (%)	Cone 08 (%)
N. C. feldspar	6	0.155	0.089	0.00	
	9	0.113	0.093	0.078	0.00
Flint	6	0.009	0.009	0.00	
	9	0.002	0.00		
1	6	0.089	0.020	0.00	
	9	0.067	0.015	0.00	
2	6	0.102	0.020	0.00	
	9	0.091	0.020	0.00	
3	6	0.118	0.025	0.00	
	9	0.111	0.025	0.00	
4	6	0.133	0.029	0.00	
	9	0.115	0.030	0.00	
5	6	0.140	0.034	0.00	
	9	0.123	0.035	0.00	
6	6	0.146	0.039	0.00	
	9	0.131	0.039	0.00	
7	6	0.151	0.044	0.00	
	9	0.133	0.041	0.00	
Ga. kaolin	6	0.044	0.020	0.00	
	9	0.012	0.00		
9	6	0.066	0.034	0.015	0.009
	9	0.059	0.049	0.039	0.030
10	6	0.075	0.039	0.015	0.009
	9	0.069	0.059	0.049	0.030
11	6	0.084	0.049	0.030	0.025
	9	0.073	0.065	0.058	0.034
12	6	0.090	0.054	0.043	0.030
	9	0.078	0.069	0.058	0.038
13	6	0.097	0.069	0.054	0.044
	9	0.086	0.078	0.064	0.039
14	6	0.187	0.162	0.138	0.044
	9	0.098	0.083	0.064	0.012
15	6	0.207	0.165	0.143	0.044
	9	0.150	0.113	0.081	0.015
16	6	0.224	0.172	0.152	0.074
	9	0.101	0.079	0.055	0.010
17	6	0.244	0.177	0.156	0.089
	9	0.120	0.098	0.064	0.015

II. Results and Discussion

The percentage linear expansions of the mixtures, after they were autoclaved and dehydrated to various temperatures, are given in Table V. Of the three end

materials, at both the cone 6 and cone 9 firings, the feldspar had by far the greatest moisture expansion.

In all three series of mixtures, the moisture expansion for all of the bodies fired to cone 9 was less than for the corresponding body fired to cone 6. In the feldspar-Georgia kaolin series, at both cones 6 and 9, the expansion increased with the increase of feldspar although the absorption decreased correspondingly. This same condition existed in the feldspar-flint series at cone 6, although the absorption remained practically constant throughout the series. In the cone 9 feldspar-flint series, there was no relation between the moisture expansion and the feldspar-flint ratio. Body No. 15 showed an abnormal expansion, although the absorption for this body is close to the value expected.

From these data it appears that, within the ratios studied and giving absorption values far removed from vitrification, the addition of feldspar to a clay-flint body is a contributing factor to its moisture expansion.

The Georgia kaolin-flint series, fired to cones 6 and 9, had much greater moisture expansion than the materials themselves, although the absorption values for all of the bodies at cone 6 were practically the same.

As in Part I, combinations possibly containing excessive amounts of flint did not return to their original dimensions even when they were heated to cone 08, whereas those composed of clay and feldspar and having no free flint returned to their original lengths when they were heated only to 700°C.

The data obtained in investigating all three series of combinations, Georgia kaolin-feldspar, Georgia kaolin-flint, and feldspar-flint, are not sufficient to justify any conclusion as to whether moisture expansion in a porous body is caused by absorption, adsorption, chemical combination, or solid solution effects.

Acknowledgment

The writer wishes to express his appreciation to H. C. Harrison of the Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa., for his cooperation in securing a number of test specimens fired at cone 11 in the Company's tunnel kiln.

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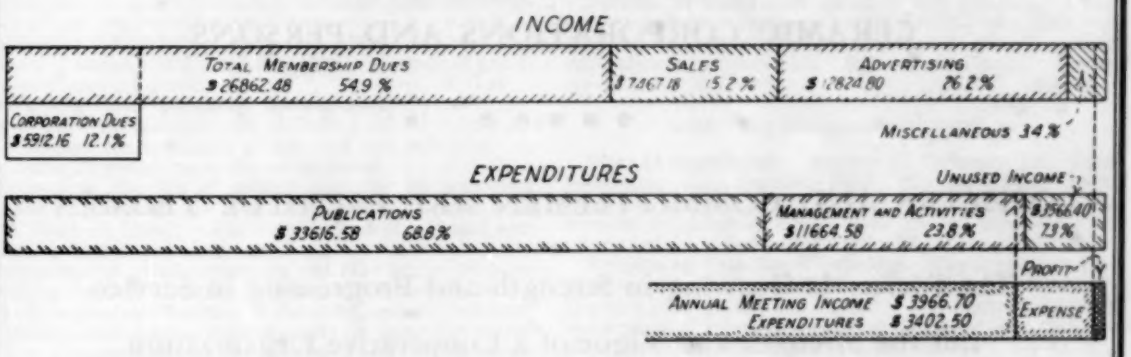

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February, 1941
20—2

Abrasives

Causes and prevention of grinding cracks. J. C. ALEXANDER. *Machinery* [London], **51** [1308] 130–31 (1937).—A. discusses the causes and prevention of grinding cracks, the depth of crack penetration, and the resistance of tool steel to abrasion. F.G.H.

Grinding detachable rock-drill bits. ANON. *Machinery* [London], **50** [1294] 543 (1937).—Details of grinding technique are given. F.G.H.

Grinding and polishing for micrography. W. H. DEARDEN. *Metallurgist*, **10**, 157–59, 162–64 (1936).—D. discusses the technique of grinding and polishing. A few notes on mounting media are included. F.G.H.

Increasing the life of cutting tools by an improved method of grinding. L. J. C. *Machinery* [London], **56** [1447] 431–34 (1940).—The new method of grinding and polishing high-speed steel and Stellite tools involves (1) maintenance of proper clearance and rake angles through quadrant control, (2) rough-grinding of the tools in such a way as to eliminate burning or checking, and (3) polishing of the clearance and top rake angles to eliminate the coarse cutting edge produced by the grinding wheel and the rough surface on the top face of the cutting tool which causes excessive frictional heat as the flowing chip slides over it. F.G.H.

Lapping. F. W. SHAW. *Machinery* [London], **53** [1373] 559–61 (1938).—S. discusses the influence of lapping on the durability and efficiency of coacting metal surfaces. F.G.H.

Lapping process—abrasives and wheels employed. A. J. SCHROEDER. *Machinery* [London], **56** [1446] 404–405 (1940).—S. discusses the features which characterize the lapping process and describes the applications of various types of abrasive wheels. F.G.H.

Nature of lapped and polished surfaces. FRANCIS W. SHAW. *Machinery* [London], **50** [1289] 389–92 (1937).—S. analyzes a controversy between various authors in connection with results of experiments with the Shaw Contorograph. See "Finishing . . . ," *Ceram. Abs.*, **15** [9] 265 (1936); "Surface . . ," *ibid.*, **19** [10] 227 (1940). F.G.H.

Roll grinding. H. J. W. *Machinery* [London], **42** [1080] 343–45 (1933).—Fundamental principles of roll grinding are briefly discussed. F.G.H.

Sources of waste-heat losses in fine grinding. LEONARD ANDREWS. *Engineer*, **166** [4329] 745–46 (1938).—A. discusses the subject from the standpoints of both wet and dry grinding. Illustrated. See "Classified. . . ," *Ceram. Abs.*, **19** [1] 19 (1940). F.G.H.

BOOKS AND SEPARATE PUBLICATIONS

Story of Superfinish. ARTHUR M. SWIGERT, JR. Lynn Publishing Co., Detroit, 1940. 672 pp. Price $5.00. Reviewed in *Mech. Eng.*, **62** [12] 922 (1940).—A chapter devoted to abrasives covers their history from early development up to the use of bonded abrasives. F.G.H.

Treatise on Tool-Room Grinding. CARBORUNDUM CO., Manchester, England, 1936. Reviewed in *Machinery* [London], **54** [1392] 348 (1939).—The characteristics of many types of grinding wheels are described, and their application in the tool room is discussed. F.G.H.

Uses of Lac. H. K. SEN AND S. RANGANATHAN. Indian Lac Research Inst., Namkum, Ranchi, Bihar, India, 1939. 78 pp. Price Re 1, 4 annas. Reviewed in *Ind. Eng. Chem., News Ed.*, **17** [22] 717 (1939).—The use of shellac in the production of grinding wheels is described. F.G.H.

PATENTS

Abrasive. A. J. WEINIG. U. S. 2,224,711, Dec. 10, 1940 (Jan. 16, 1939).—A dry abrasive for fine grinding comprises a dry mixture of powdered silicon carbide, powdered flint, and precipitated copper hydroxide, the grain size of the silicon carbide not exceeding 20 microns and the grain size of the flint not exceeding 5 microns in size.

Abrasive article. W. P. FITZ-RANDOLPH (Carborundum Co.). U. S. 2,223,063, Nov. 26, 1940 (Oct. 7, 1937; Sept. 1, 1939).—A metal-bonded abrasive article consists of abrasive grain and a metal bond therefor comprising a sintered mixture of metal powders including zinc powder and not

more than about 30% iron powder, at least a substantial portion of the zinc and iron being alloyed.

Abrasive article and method of making. R. L. Smith (Carborundum Co.). U. S. 2,223,392, Dec. 3, 1940 (May 10, 1937).—An abrasive article comprises abrasive grains and a binder for the grains comprising a thermal reaction product of a phenolic resin with an alkali.

Abrasive article and method of manufacturing. J. B. Aust (Carborundum Co.). U. S. 2,224,009, Dec. 3, 1940 (Feb. 24, 1939).—A water-resistant coated abrasive product.

All-purpose grinding apparatus. A. W. Mall. U. S. 2,223,732, Dec. 3, 1940 (Oct. 10, 1936).—An apparatus for grinding rails.

Apparatus for dressing abrasive wheels. J. E. Miane. Fr. 841,936, Aug. 9, 1938. D.A.B.

Apparatus for forming or dressing the operative faces of grinding wheels. Coventry Gauge & Tool Co., Ltd., S. J. Harley, and J. E. Wainwright. Brit. 527,654, Oct. 23, 1940 (April 18, 1939).

Automatic grinding machine. Norton Co. Fr. 844,274, Oct. 4, 1938. D.A.B.

Buffing edges of metal fasteners. F. B. Smithe and Abraham Novick (F. L. Smithe Machine Co., Inc.). U. S. 2,221,885, Nov. 19, 1940 (Jan. 27, 1937).

Cloth or fiber base or support for abrasive. J. Bontus. Fr. 842,717, Feb. 23, 1938. D.A.B.

Eccentric head for cam grinding pistons. Eric Edwin and Merle Peterson. U. S. 2,221,080, Nov. 12, 1940 (March 7, 1939).

Gear-grinding machines. Soc. Anon. de Rectification et d'Engrenages Procédés Minerva. Brit. 528,488, Nov. 13, 1940 (May 13, 1938).

Grinding or abrading machines. Coventry Gauge & Tool Co., Ltd., and S. J. Harley. Brit. 528,902, Nov. 20, 1940 (March 8, 1939).

Grinding machine. Horstman; Ltd. Fr. 840,525, July 9, 1938. Maschinenfabrik Wafios, Wagner Ficker und Schmidt. Fr. 829,444, Nov. 18, 1937. Norton Co. Fr. 841,766, Aug. 5, 1938. D.A.B.

Grinding machine. J. V. Bergfeldt. U. S. 2,222,580, Nov. 19, 1940 (July 27, 1938). H. S. Indge (Norton Co.). U. S. 2,221,638, Nov. 12, 1940 (June 15, 1940). C. R. Williams (Atlantic Service Co., Inc.). U. S. 2,222,966, Nov. 26, 1940 (Dec. 16, 1938).—A grinding machine comprises a housing with a pair of belt wheels therein.

Grinding machine for metals. A. Ghaye, E. Spiers, T. A. Spiers, and W. Spiers. Fr. 826,992, Sept. 21, 1937. D.A.B.

Grinding machine, more particularly for grinding gears. Soc. Anon. de Rectification et d'Engrenages Procédés Minerva. Brit. 528,489, Nov. 13, 1940 (May 13, 1938).

Grinding and polishing machine. Friedrich Zeissl. U. S. 2,222,454, Nov. 19, 1940 (July 7, 1936).

Grinding wheel. W. P. Leshure (A. L. Bausman). U. S. 2,223,326, Nov. 26, 1940 (Feb. 7, 1939). Norton Grinding Wheel Co., Ltd. Brit. 528,834, Nov. 20, 1940 (May 19, 1938).

Grinding wheels. Compagnie des Meules Norton, Soc. Anon. Fr. 829,132, Nov. 16, 1937. D.A.B.

Grinding wheel truing apparatus. Norton Co. Brit. 528,225, Nov. 6, 1940 (May 4, 1938).

Honing apparatus. H. S. Indge (Norton Co.). U. S. 2,221,637, Nov. 12, 1940 (Dec. 14, 1939).

Improvements on grinding and polishing wheels. S. W. Lippitt. Fr. 830,188 to 830,190, Nov. 30, 1937. D.A.B.

Machine for grinding circular saw blades. K. Wagner. Brit. 528,021, Oct. 30, 1940 (April 26, 1939).

Machine for grinding crankshafts. H. S. Indge (Norton Co.). U. S. 2,221,260, Nov. 12, 1940 (Nov. 26, 1938).

Machine for grinding surfaces of an oval section. Mayer und Schmidt Schleifmaschinen und Schmirgelwerke A.-G. Fr. 827,071, Sept. 23, 1937. D.A.B.

Manufacturing abrasive articles. Norton Grinding Wheel Co., Ltd. Brit. 528,563, Nov. 13, 1940 (Jan. 28, 1938).

Manufacturing grinding tools containing diamond. G. Barth-Vuilleumier. Fr. 828,159, Oct. 21, 1937. D.A.B.

Needle-eye polishing machine. Singer Mfg. Co. and E. Rohloff. Brit. 528,390, Nov. 13, 1940 (April 29, 1939); addition to 400,095.

Objects containing silicon carbide. Carborundum Co. Fr. 836,900, April 20, 1938. D.A.B.

Producing abrasives. I. G. Farbenind. A.-G. Fr. 841,814, Aug. 6, 1938. D.A.B.

Sanding or polishing wheel. R. S. Gutsell. U. S. 2,221,173, Nov. 12, 1940 (Aug. 6, 1938).

Screw-thread grinding machines. Hopkinsons, Ltd., and T. Metcalfe. Brit. 527,785 and 527,829, Oct. 30, 1940 (April 15, 1939).

Sharpening device for edged implements. J. E. Burns. U. S. 2,222,361, Nov. 19, 1940 (Nov. 1, 1939).

Spindle and bearing therefor. Bryant Chucking Grinder Co. Brit. 528,003, Oct. 30, 1940 (July 7, 1938).

Surface grinding machine. Maschinenfabrik H. Hauser Akt.-Ges. Brit. 528,218, Nov. 6, 1940 (July 2, 1938).

Valve-grinding machine. E. A. Hall and K. R. Bohn (Hall Mfg. Co.). U. S. 2,221,918, Nov. 19, 1940 (Oct. 21, 1938).

Work-rotating devices for grinding machines and other machine tools. F. Deckel (trading as F. Deckel Prazisions-Mechanik & Maschinenbau). Brit. 528,887, Nov. 20, 1940 (June 2, 1938); addition to 504,245, May 3, 1939. Brit. 528,888, Nov. 20, 1940 (June 10, 1938); addition to 504,245

Art and Archeology

Cup-shaped glasses and stemware. Bruno Mauder. *Glashütte*, 70 [33] 417–19 (1940).—Drinking receptacles played a definite part in the production of glass. Bowls were used for drinking in ancient times; from the bowl were derived the cup and finally the cup-shaped glass. Form was always subordinate to technique, and a discussion of form would include the entire process of glassmaking. Later, the cup acquired a base with a band of glass placed between these two parts, and this band developed into an intermediate part or stem. This transformation was brought about by the increasing development of the technique of glassmaking which permitted more elaborate forms of expression. The Roman form of drinking glass appeared. In the transition period, crystal glass with a smooth tulip-formed cup, a ring-shaped intermediate part, and a smooth bell-shaped foot was made of green glass of the "forest glass" period. The Venetians, with their advanced technique, produced the elegant goblet with beautifully curved cup and stem, the base being raised in the center. This glass had no ornamentation and served as the model for all future types. Early German crystal goblets were massive and solid. The earliest goblets were worked by hand, as was all glass until the introduction of large-scale production which made possible exact reproductions of uniform height and form. Parts were blown separately and then attached. Wood was used as fuel. Many parts could be combined, and bands, threads, and other trim were applied. Later, the cup shape was emphasized more. The intermediate piece was frequently reduced to a juncture of the cup and the base, thereby completely altering the appearance of the glass. The height of wine glasses was varied. Many forms were adopted: cylindrical, conical, globelike, egg-shaped, and bell-shaped. The roll- or ball-shaped connecting piece was gradually discarded, and the cup stood directly on the stem. The form of the stem also varied, the smooth stem of

uniform thickness predominating in cheaper stemware; for bell- or tulip-shaped cups, a bulge in the center or upper part of the stem was more suitable. Wedge-shaped stems, those formed of balls or ovals, and hollow, ribbed, and colored-inlay stems became less frequent. The foot was only slightly changed; it was usually smooth and somewhat raised in the center. Medium-tall styles replaced the tall glasses, and low types with a short stem reappeared. The thickness of lead crystal glass permitted deep cutting on the stem and the cup, but thick glasses were gradually replaced by thinner ware. Engraving is popular today, but with the exception of the gold band, colored glasses are not in demand. Modern styles of (1) smooth goblets, (2) cylindrical cups and their decoration, (3) conical forms and arrangement of the trim, (4) cups developed from globes, and (5) cut-glass models are illustrated. A complete monograph on the development of stemware with illustrations from all periods is in preparation and will soon be published. M.V.C.

Glass design at Carnegie Institute of Technology. ANON. *Glass Ind.*, **21** [11] 478–81 (1940).—Graduates of the four-year course in industrial design are influencing design in the various fields of glass by the use of the fundamental principle of "breakdown." 8 illustrations. A.P.

How I came to take an interest in pottery. CONRAD DRESSLER. *Bull. Amer. Ceram. Soc.*, **19** [12] 484–86 (1940).

System in color preferences. J. P. GUILFORD. *Jour. Optical Soc. Amer.*, **30**, 455–59 (1940).—Three hundred sixteen color specimens were rated for pleasingness by 100 observers. Preferences were related to lightness, saturation, and Munsell value and chroma. A.P.

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Designs for:

Bake pan. JACK KOLLMAN (Edward Katzinger Co.). U. S. 123,504, Nov. 12, 1940 (May 27, 1940).

Bottle. B. D. FUERST (Owens-Illinois Glass Co.). U. S. 123,499, Nov. 12, 1940 (Sept. 7, 1940). P. G. LLOYD (Carr-Lowrey Glass Co.). U. S. 123,621, Nov. 19, 1940 (May 24, 1940).

Bowl for lighting fixtures. T. W. ROLPH (Holophane Co., Inc.). U. S. 123,765, Dec. 3, 1940 (Oct. 5, 1940).

Glass jug. W. J. LUNDY (Olean Glass Co.). U. S. 123,505, Nov. 12, 1940 (Aug. 23, 1940).

Glass tumbler. A. J. DREITZER (Pitman-Dreitzer & Co., Inc.). U. S. 123,858, Dec. 10, 1940 (Oct. 3, 1940).

Goblet. L. C. KELLEY. U. S. 123,598, Nov. 19, 1940 (Aug. 26, 1940).

Milk bottle. W. C. TEUNISZ. U. S. 123,965, Dec. 10, 1940 (April 22, 1939).

Cements

SEPARATE PUBLICATIONS

High-Alumina Cement. *British Standard Specification*, No. 915 (1940). British Standards Inst., London. Price 2s.—The following requirements are specified: (1) Fineness: the residue on a B.S. No. 170 sieve (0.0035-in. aperture) shall not exceed 8%. (2) Composition: the cement shall contain not less than 32% of alumina. The ratio of alumina:lime (by weight) shall be between 0.85 and 1.3. (3) Compressive strength: the compressive strength of 2.78-in. cubes composed of cement 190, standard sand 570, and water 76 parts shall be (*a*) after 1 day, not less than 6000 lb. per sq. in., and (*b*) after 3 days, not less than 7000 lb. per sq. in. (4) Setting time: the initial setting time shall be between 2 and 6 hr.; the final setting time shall be not more than 2 hr. after the initial set. (5) Soundness: the expansion in a Le Châtelier gauge shall not exceed 1 mm. The compression test is preferred to a tensile test because the results obtained by different gauges agree more closely and the strength of the cubes can be related to that of concrete made with the same cement. A.B.S.

Portland Cement and Rapid Hardening Portland Cement. *British Standard Specification*, No. 12 (1940). British Standards Inst., London. Price 2s. A.B.S.

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Cement with a soluble silicate base. L. TOURNIER. Fr. 828,801, Feb. 3, 1937. D.A.B.

Colored cements and process of production. P. GERIMONT. Fr. 825,759, Aug. 19, 1937. D.A.B.

Coloring cement articles. I. G. FARBENIND. A.-G. Fr. 826,373, Sept. 4, 1937. D.A.B.

Preparing cements resistant to acids. I. G. FARBENIND. A.-G. Fr. 842,342, Aug. 20, 1938. D.A.B.

Enamel

Damage from smoke in the enamel industry. ANON. *Glashütte*, **70** [35] 461 (1940).—Hydrofluoric and sulfuric acids are the chief waste gases which cause damage to vegetation in the vicinity of enamel factories. When enamels are fused, the fluorine opacifiers (cryolite, sodium fluosilicate, fluorspar, etc.) react with silica to form the volatile silicofluoride. In a tank furnace these reactions proceed slowly, and the gases seldom escape in sufficient quantities to cause damage; in a revolving furnace, however, where the melt is continually rotated, there is a closer contact between the melt and the gases with the result that the fluorine gases are not taken up by the melt but escape through the stack. Since water is also present, the gas combines with it to form fluosilicic acid which injures leafy vegetation. Leaves become speckled with brown, and the edges turn yellow; rye and wheat are especially sensitive to this acid. Glass windowpanes of the plant are also etched by this acid in the atmosphere. Two remedies are as follows: (1) The melting process in a revolving furnace should be conducted so as to correct the fusion reactions. (2) The ordinary sheet-metal stack which rises above the roof should not be used for waste gases. Besides fluosilicic acid, sulfurous acid derived from the combustion of coal or oil containing sulfur is also a cause of complaint. The length of time that vegetation is exposed to these noxious gases is another determining factor. The waste gases can be diluted with moving quantities of fresh air. The use of "latticed" stacks permits the hot gases to mix with the cold air which streams through the holes in the stack. M.V.C.

Enameling de-enameled sheet-metal objects. H. LANG. *Glashütte*, **70** [33] 420–21 (1940).—Both chemical and mechanical methods of de-enameling sheet-steel objects may injure the surface of the metal to such an extent that successful re-enameling is difficult. Theoretically, hydrofluoric acid does not affect iron, but it is found from experience that the metal is blackened, supposedly from the mud in the acid bath, and it is almost impossible to clean off this black completely, even by pickling. Some chemical reaction has occurred which has penetrated the inside of the metal and loosened layers of oxide, especially in thin places in the metal. This roughens the surface to such an extent that many defects, such as a special kind of copperhead, corroded spots, and devitrification, appear in the ground enamel, making necessary the application of a second ground coat; the enamel may also break off, showing the silver metal beneath. These defects can be prevented by subjecting the metal to severe burning followed by strong pickling in HCl, but care must be taken to avoid the well-known consequences of strong pickling. This

treatment, as well as the hydrofluoric acid itself, tends to make the metal brittle. Other chemical methods of de-enameling use (1) a mixture of hydrofluoric and sulfuric acid, or (2) caustic soda, both of which corrode the metal and cause the flaws already mentioned. Especially is this true of the first method, because the sulfuric acid attacks iron after the hydrofluoric acid has dissolved the enamel. Another defect of de-enameled sheet metal is the so-called pickling or sheet-metal blisters which may be removed in the manner explained (if they are not large) or perforated and flattened provided they are noticeable before enameling. All the flaws mentioned are increased when de-enameling baths under pressure are used. Mechanical de-enameling by blasting with steel filings or sand causes the fewest difficulties and is cheaper; pickling blisters never occur. It is the preferred method, its chief drawback being that the surface of the metal may be injured, roughened, or torn unless great care is exercised. The rougher the surface of the metal, the more difficult it is to cover it with enamel, and frequently two ground coats or a much thicker single ground are required to completely cover the metal and produce a good cover coat. It is best to smooth up the surface of the metal by burning, pickling, sandpapering, and polishing before applying the ground enamel. M.V.C.

Genesis of pearlite and martensite. FRANKLIN H. ALLISON, JR. *Metal Progress*, **36** [1] 60–65 (1939).—A. gives an explanation of the famous "S" curve for plain carbon eutectoid steel. The nodules of "primary troostite" are made up of fine pearlite. A little-known acicular constituent forms directly from austenite at subcritical temperatures ranging from about 900° down to 300°F. A discussion of the transformation into martensite is given. Charts and tables. J.J.H.

Prevention of loss of materials in enamel plants. H. LANG. *Glashütte*, **70** [30] 373–75 (1940).—Loss and waste of materials used in enameling can be greatly reduced by strict supervision of workmen and apportionment of the materials used in each operation. A method for preventing unnecessary waste was worked out, which, although not new, was found to improve conditions: (1) For a given operation where any raw material is used, the smallest quantity needed must be determined exactly in advance. (2) This quantity must be rigidly adhered to by the workmen. (3) The worker must be held responsible for maintaining this minimum and must be answerable for the materials. (4) Every separate operation must be standardized and controlled. (5) A constant automatic control should aid the worker or overseer and afford a means of checking. The efficacy of this method is discussed in the case of spraying enamel, where unbelievable quantities of enamel are wasted. The minimum quantity of enamel required for a given piece and the amount of enamel the sprayer needs in his gun must be determined exactly and adhered to by the workers. This "coefficient of work" should be determined for all branches of enameling, e.g., in the fusing, grinding, and dipping processes, etc. It is frequently found that higher output is accompanied by greater waste, and it is preferable to reduce output to save on material, since the latter is the expensive factor. The sprayer should fill his gun from measuring cups which indicate the exact amount of enamel needed for a given piece. The sprayer will eventually learn the amount of enamel to use in each case, but the work must nevertheless be constantly watched and checked by the overseer. To prevent ill-feeling among the workers, the purpose of such care and its advantages to them must be fully explained. Tables which show the total quantity of enamel, its consistency, and other data, placed where the workers can see them, awaken interest. The estimation of the quantity of each material needed, the delivery of only the necessary minimum, and constant supervision to enforce this economy are the most important duties of the overseers. By this means causes and sources of loss of materials can be ascertained, and abuses can be corrected. The enamel slip must be kept at the proper consistency, and fineness of grinding, viscosity, and other factors should be constantly controlled. M.V.C.

Raw materials for sheet enamel. HEINRICH KIRST. *Glashütte*, **70** [34] 448–49 (1940).—Raw materials which may be used to replace borax in enamels that are not to be used for cooking utensils are (1) zinc oxide, (2) barium compounds, (3) strontium compounds, (4) barium and strontium fluorides, (5) magnesia, (6) potash, (7) titanic acid, and (8) antimony compounds. Zinc oxide for enamels must be free from metallic zinc. It imparts a low expansion to the enamel and has a favorable action on the tensile strength and resistance to pressure. Zinc oxide has a low specific gravity which may impair the elasticity of enamels, but it has a good fluxing action. It is not used as an opacifier, but it lowers the solubility of opacifiers in the enamel. Zinc oxide can be used for white cover enamels and for colorless transparent coats for colored enamels in additions of 5 to 10%. It is especially good for ground enamels with a low borax content. The form of barium most often used in enamels is the artificially produced barium carbonate, because of its purity. With its high molecular weight, barium carbonate gives a luster to enamel and improves its chemical and physical properties, especially the elasticity. Barium oxide has the same effect as lead oxide on expansion and is a good flux. An addition of 10% is customary, and it can be used for ground and cover enamels. Barium nitrate is employed in enamels for refining and purifying, as are potassium or sodium saltpeter, because of the oxidizing action of the nitrate. Strontium oxide is harmless; it has an effect similar to that of barium oxide and is usually used in combination with it. Strontium nitrate and especially strontium carbonate are the raw materials. Barium and strontium fluorides as raw materials for enamels have a good fluxing action and resemble calcium fluoride in behavior. At present they are not produced in large quantities, but their manufacture presents no difficulties. Magnesium oxide has not been used extensively for enamels, but it is harmless and improves the thermal and chemical properties of enamels. Because of the difficulty of fusing, it can be used only in amounts of 2 to 3%. It is especially good for ground enamels but can also be used for cover enamels. Magnesium carbonate dissolves in the melt more easily than the oxide. Potash is frequently replaced by the cheaper soda, but it has a better action on the thermal properties of enamels than soda; it should be used in greater amounts in enamels with low borax content, therefore, and the difference in cost is compensated by the saving in borax and by the improvement in results. The joint use of potash and soda improves the melting and fusibility of the enamel. Potassium nitrate or potassium carbonate are the raw materials. The materials mentioned above serve as basic constituents in enamels, while titanic acid is an acid oxide for enamels and is especially suitable as a substitute for borax and boric acid. Titanic acid augments the softening interval of the enamel and makes the melt viscous. It is present in sufficient quantities in pure form, but precautions against iron oxide impurities must be taken. It is used for ground and cover enamels, and it raises the expansion of the enamels only slightly. M.V.C.

BOOKS AND SEPARATE PUBLICATIONS

Bibliography on Enameling. G. T. O. MARTIN. Joint Committee on Vitreous Enameling, Birmingham, England. 100 pp. Price 15s.—This annotated bibliography on vitreous enameling provides a record of the chief literature on the subject published in recent years up to July, 1939, when *Enamelling Abstracts* first appeared. L.R.B.

Glossary of Terms in Use in the Vitreous Enameling Industry. G. T. O. MARTIN. Joint Committee on Vitreous Enameling, Birmingham, England. 10 pp. Price 1s.—One hundred forty-three terms used in the literature of vitreous enameling are defined. L.R.B.

PATENTS

Apparatus and process for producing relief or hollow designs on enameled objects. SOC. FRANÇAISE DES FERS EMAILLÉS. Fr. 828,827, Feb. 5, 1937. D.A.B.

Dry method of enameling. Vereinigte Chemische Fabriken Kreidl, Heller & Co., A.-G. Fr. 844,759, Oct. 15, 1938. D.A.B.

Preparation of opaquing agents for white enamels. Soc. de Produits Chimiques des Terres Rares. Brit. 528,321, Nov. 6, 1940 (May 5, 1938).

Producing enameled objects. Aciérie & Laminoirs de Beautor. Fr. 842,661, Feb. 18, 1938. D.A.B.

Producing silica base enamels opacified with zirconium oxide. Auerges. A.-G. Fr. 843,478, Sept. 14, 1938. D.A.B.

Vitrifying or enameling objects or any surface. Soc. Nouvelle de Métallisation. Fr. 843,064, March 2, 1938. D.A.B.

Glass

Absorption behavior of neodymium in glasses. Gottfried Rosenthal. *Glastech. Ber.*, **18** [6] 155–58 (1940).—The Nd_2O_3 content was varied from 5 to 15% in glasses with 15% of alkali oxide and 10% of alkaline-earth oxide. Silica, borosilicate, borate, and phosphate glasses were examined. Spectrograms were obtained on Agfa 950 infrared plates and evaluated by means of a Zeiss registering photometer and Abbe comparator. The results are presented as curves plotting log of transmission against wave length. Variations due to changes in the Nd_2O_3 content or to the secondary constituents were not observed in the spectral range studied. A change of the glassforming oxide causes a shift in the wave length of minimum transmission: silica 8795 a.u., borosilicate 8780 a.u., borate 8750 a.u., and phosphate 8737 a.u. The curves for the glasses show a flat spot on the short wave length side of the minima. A similar flat spot occurs on the long wave length side of the transmission minima, 8645 a.u., of aqueous $Nd(NO_3)_3$ solutions. R. concludes that glasses containing two glassforming oxides such as the borosilicates are not merely mixtures but that both oxides are simultaneously involved in forming the network. J.F.H.

Bibliography of glass electrodes. Ludwig Kratz. *Z. Elektrochem.*, **46** [4] 259–64 (1940).—The bibliography covers the literature from 1880 to 1939 (385 references). J.M.N.

Corning's Vycor patents. Anon. *Glass Ind.*, **21** [11] 482–83 (1940).—The features of the product and process patents issued to H. P. Hood and M. E. Nordberg covering "shrunk glass," sold as 96% silica or Vycor, are summarized. A.P.

Density of silicate glasses as a function of composition. M. L. Huggins. *Jour. Optical Soc. Amer.*, **30**, 420–30 (1940).—In a well-annealed silicate glass, the volume per gram of oxygen is given quite accurately by the equation $V_o = k + b_{Si} + c_{Si}N_{Si} + \Sigma c_M N_M$, where k is a very small constant characteristic of the annealing technique, N_{Si} and N_M are the numbers of Si or other "metal" atoms per atom of oxygen, b_{Si} and c_{Si} are constants which differ for different ranges of N_{Si} values, and c_M values are constants valid for all values of N_M as far as can be determined from present data. For boron-containing glasses, separate terms are required for tetrahedrally surrounded and for triangularly surrounded atoms, the relative numbers of which depend on the relative amounts of Si, B, and O. With the aid of the above equation, densities can be calculated from compositions simply and accurately. The empirical results are interpreted theoretically from the packing of oxygens and hypotheses made about the positions in the framework of boron, magnesium, aluminum, and titanium. See "Refractive. . . ," p. 42. A.P.

Determination of the protective capacity of bottles against light. Hans Freytag. *Glastech. Ber.*, **18** [6] 147–55 (1940).—The method of exposing a photosensitive material to light through glass was examined for the purpose of developing a suitable standard method. The Eder solution consisted of 1.0 gm. ammonium oxalate in 250 cc. water, 1.0 gm. mercuric chloride in 250 cc. water, and 10% aqueous ferric chloride. The solutions were stored in the dark. A suspension of 0.5 gm. cornstarch in 250 cc. water with a little phenol served to compare turbidities, 10 cc. being diluted to 50 cc. for use. A determination was carried out by mixing 3 cc. of each of the first two reagents in a test tube equipped with a small wire stirrer, adding two drops of ferric chloride, and measuring the time required to develop the same turbidity on exposure to daylight under the same conditions. The ratio of the time of insertion in the test bottle to the time on exposure without the bottle was taken as a measure of the absorption of the flask. The method makes it possible to classify glasses in three groups with ratios of 0 to 2, 3 to 4, and > 5 but is not entirely satisfactory. A simpler and more satisfactory procedure was developed, using a selenium photocell, which makes possible the determination of the absorption in various spectral ranges with good reproducibility. A light beam was passed through a filter, through the bottle to be tested, and into the photocell attached to a sensitive ammeter. An average reading was obtained by rotating the bottle. The absorption (%) was calculated by the use of Lambert's absorption law. Jena filters UG1/2, BG6/1, VG3/2, and VG3/1 were used in this work. J.F.H.

Effect of time and temperature on accelerated chemical durability tests made on commercial glass bottles: II. F. R. Bacon and O. G. Burch. *Jour. Amer. Ceram. Soc.*, **24** [1] 29–35 (1941).—11 tables, 10 references. For Part I see *ibid.*, **23** [1] 1–9; [2] 56 (1940).

Eye protection in high-temperature operations. Raymond R. Butler. *Engineer*, **166** [4303] 24–25 (1938).—B. discusses the manufacture of glasses for protecting the eyes from harmful radiations. The protective properties of various glasses are discussed. Illustrated. F.G.H.

Fiberglas—a new basic raw material. Games Slayter. *Ind. Eng. Chem.*, **32** [12] 1568–71 (1940).—Glass fibers possess desirable properties not found in any other commercially available material. They are produced as a woollike fiber largely used for thermal insulation and as a textile fiber, either continuous or in staple lengths, employed to form yarns, threads, and woven fabrics. Glass fibers are inorganic, incombustible, and nonabsorptive. They possess extraordinary tensile strength, electrical properties, and heat resistance. They are chemically stable and resist attacks of many chemicals. They do not rot, decay, or feed fungus growths or vermin. Colors in the glass itself are sunfast and durable; dyes may be used for surface coloring of the fibers. Wool forms are used for insulation of houses, ships, trains, aircraft, ranges, refrigerators, etc., and for industrial insulation at temperatures from below 0° to over 1000°F. Textile forms are used for electrical insulation, electric storage battery retainer mats, chemical and fume filtration services, and a wide variety of industrial applications. Decorative fabrics have found many practical applications. Glass fabrics are not recommended for wearing apparel. Illustrated. F.G.H.

Glass Container Assn. annual meeting. Anon. *Glass Ind.*, **21** [11] 475–76 (1940).—Accomplishments resulting from the activities of the staff of the Glass Container Assn. are reported. A.P.

Glass-insulated motors for machine tools. Anon. *Machinery* [London], **55** [1418] 285 (1939).—The characteristics and advantages of glass insulation are described in detail. F.G.H.

"History of Glass" from the World's Fair donated to the Chicago Museum. Anon. *Glass Ind.*, **21** [11] 486 (1940).—The series of twenty glass retorts containing carved miniatures that depict the growth of glassmaking and the series of eight animated displays demonstrating the char-

acteristics and properties of glass have been permanently donated to Chicago's Museum of Science and Industry. 20 photographs with legends. A.P.

Hollow glass blocks as building material. ANON. *Engineer*, **162** [4218] 510–11 (1936).—Methods of manufacture, physical characteristics, and uses are described. Illustrated. F.G.H.

Improving the strength of glass containers through design. L. G. GHERING. *Glass Ind.*, **20** [12] 443–47, 472 (1939).—G. discusses definitely established general principles with respect to bottle design and its relation to strength under the following headings: (1) theoretical aspects of design for economy of material, (2) economy of glass in practice, (3) theoretical effect of shape on strength, (4) practical aspects of strength and design, (5) internal pressure strength in practice, (6) practical design for high thermal-shock strength, (7) effect of design on impact strength, and (8) relation of distribution and design to lighter weight. A.P.

Indian glass industry. K. R. GANAPATHY. *Ind. Eng. Chem., News Ed.*, **15** [24] 546 (1937).—All Indian glassware is of the soda-lime variety. Lead and potash glasses are not made because of the high price of red lead, litharge, and potassium carbonate, none of which is a strictly indigenous product, although red lead and litharge are made in Calcutta from Burma lead. All raw materials required for the production of soda-lime glass, with the exception of soda ash, are found in abundance in India. F.G.H.

Inhomogeneities in glass leading to breaks derived from refractories above the melt. H. JEBSEN-MARWEDEL. *Glastech. Ber.*, **18** [6] 160–62 (1940).—Breaks in flask walls have been traced to inhomogeneities resulting from the slagging of unsuitable refractories. J.F.H.

Making molds at Swindell Brothers, Inc. ANON. *Glass Ind.*, **21** [11] 471–74 (1940).—The small size, large variety, and great number of items produced at the Swindell Brothers plant in Baltimore require a sizable, well-equipped shop for the manufacture and repair of molds. 13 photographs. A.P.

Measurement of strain in glass. J. G. HOLMES. *Jour. Sci. Instruments*, **17** [9] 227–28 (1940).—Stress distribution in a rectangular strip of glass subject to a uniform bending moment gives an appearance when viewed in polarized light similar to that given by quartz wedges. H. describes how this effect may be used to evaluate the unknown stresses in strained optical media. 4 figures. J.L.G.

One hundred years of mineral wool. JOSEPH STEWART AND CHARLES D. RICHARDSON. *News Ed. (Amer. Chem. Soc.)*, **18** [22] 997–98 (1940).—The fundamentals of several methods of mineral-wool production are briefly reviewed. Illustrated. F.G.H.

Polishing process in glasses. H. SCHULZ. *Glastech. Ber.*, **18** [6] 158–60 (1940).—The acid etching of ground and polished glass surfaces brings out fissures. This indicates that, along with a wearing off by the polishing agent, there is also a smoothing action resulting from deformation of some of the surface areas. J.F.H.

Reflectors used in highway signs and warning signals: I, Fundamental optical properties. G. A. VAN LEAR, JR. *Jour. Optical Soc. Amer.*, **30**, 462–71 (1940).—L. describes the fundamental properties of (reflex) reflectors, discusses their most effective use, and formulates a general basis for selecting particular reflectors for given applications. The optical function common to the various types of such reflectors (retrodirective reflection) is described, and the manner of its accomplishment by each of the two general types is explained. Brief preliminary discussions of test methods and interpretations of test results are given. **II, General basis for optical descriptions, specifications, and tests.** *Ibid.*, pp. 472–80.—The basis for giving quantitative descriptions of reflector performance in terms of specific intensity and its dependence upon the manner in which the reflector is illuminated and viewed is completed. Definitions of all special terms are tabulated and discussed. **III, Methods of measuring specific intensity.** *Ibid.*, pp. 480–87.—Preliminary consideration is given to the factors involved in the measurements. Particular methods discussed are (1) direct visual measurement with a calibrated comparison lamp, (2) an optical substitution method proposed as offering important advantages, and (3) methods using the Illuminometer and the Maxwellian view photometer. A.P.

Refractive index of silicate glasses as a function of composition. M. L. HUGGINS. *Jour. Optical Soc. Amer.*, **30**, 495–504 (1940).—Defined by a formula of either the Gladstone-Dale, the Newton, or the Lorentz-Lorenz type, the refraction per gram of oxygen equals the sum of terms characteristic of the component metallic elements. Each of these terms is proportional to the number of atoms of that element per atom of oxygen. With but little error, this is true for practically all classes of silicate glasses for which adequate data are available. Lead-containing glasses deviate from strict proportionality when the lead content is high. When the relative amount of metallic element concerned is small, constants determined from measurements on crystalline oxides can be applied. See "Density . . . ," p. 41. A.P.

Safety plate glass. G. B. WATKINS. *Glass Ind.*, **20** [12] 448–52 (1939).—The characteristics of laminated and heat-strengthened safety glasses are compared. The improvements that may be expected in laminated glass are almost infinite and will be limited only by limiting research and development work. A.P.

Symposium on glass: Glass, old and new. ALEXANDER SILVERMAN. *Ind. Eng. Chem.*, **32** [11] 1415–18 (1940).—S. presents a brief historical review. **Chemical trends.** HENRY H. BLAU. *Ibid.*, pp. 1419–23.—Chemical developments in glass technology may be logically divided into two groups: (1) those arising from the chemical relations in the formation or production of glasses, and (2) those associated with the uses of glass products. Glass compositions for general purposes have been evolved by adjustments to meet more exacting requirements in use and the needs of revised production methods. More radical measures embracing many widely different compositions have been taken to meet special technical requirements. For most purposes, fused silica glass offers almost ideal properties, which have been approached step by step in commercial glass developments. **Physical tendencies.** GEORGE W. MOREY. *Ibid.*, pp. 1423–27.—Physical trends in glass include the production of essentially new materials of greatly increased strength by controlled heat treatment, new compositions (also the result of controlled heat treatment), and new applications of glass in fields to which its properties make it especially adaptable. These new uses include architectural panels, glass building block, and the new industries built upon glass fibers. The control and enhancement of physical properties make possible these new uses and applications of glass. 4 references. **Optical characteristics.** H. R. MOULTON. *Ibid.*, pp. 1428–32.—The optical characteristics of glass are classified mainly as (1) transparency or ability to transmit radiation, and (2) refractivity or light-bending power. The effect of impurities upon transparency is discussed, with comments on the difficulties encountered by the earlier glassmakers. The necessity of accurate chemical control of batch composition and purity of ingredients in modern colored glass is emphasized. Refractivity, its importance in optical design, and methods of determining refractivity and reciprocal relative dispersion are described. New glasses of unusual refractive properties are mentioned. Surface treatment to reduce reflection and the natural and synthetic crystals which are still used in optical systems because of lack of satisfactory glasses are discussed. Improvements in glass from an optical point of view are suggested. **Silicate glasses—calculation of densities, refractive indices, and dispersions from glass composition.** MAURICE L. HUGGINS. *Ibid.*, pp. 1433–36 (1940).—Equations and constants are given for the calculation of densities, refractive indices (n_D), and dispersions ($n_F - n_C$) of silicate glasses from their compositions. For glasses in the Na_2O–SiO_2 system the average differences between calculated values and the best observed values of these properties are about 0.002, 0.00035, and 0.00007,

respectively. In general, the deviations between calculated and experimental values seem to be due largely to inadequate knowledge of the actual compositions. 12 references. Illustrated. F.G.H.

Tektites and silica glass. L. J. SPENCER. *Mineralog. Mag.*, **25** [167] 427–41 (1939).—Chemical analyses, specific gravities, and indices of refraction of 36 tektites (natural glasses) are given as collected from the literature. Plotting of the refractive indices, specific gravities, and silica contents of the glasses shows an approximately linear decrease in specific gravity and refractive index with increase in silica content. An area in the Libyan desert containing a large number of fragments of siliceous glass is described. The analyses of four specimens from this area give more than 97% SiO_2 for each of them. The origin of the fragments has not been determined. H.I.

Thin evaporated silver films on glass. JOHN STRONG AND BARRY DIBBLE. *Jour. Optical Soc. Amer.*, **30**, 431–38 (1940).—Two distinct types of films were observed. The α type is distinguished from the β type by its high efficiency, blue color by transmitted light, freedom from scattered light, and continuous variation of properties as the density of the film increases. A.P.

United States now making cover glasses. ANON. *Glass Ind.*, **21** [11] 477 (1940).—The American Window Glass Co. is producing cover glasses for microscope slides commercially. A.P.

Windows for China. SUN KUAN-HAN, J. E. FRAZIER, AND A. SILVERMAN. *Glass Ind.*, **20** [12] 453–56, 468, 470 (1939).—Flat glass may be considered the basic glass need of China. When planning a manufacturing enterprise for China, it is important to bear in mind the peculiar economy based mainly on cheap labor, coal, and land. This article is prepared from a thesis (M.S., Univ. of Pittsburgh, 1939) intended to cover every phase of constructing a sheet-glass plant in the interior of China. A.P.

Zinc oxide in the glass and enamel industries. A. FOULON. *Glashütte*, **70** [35] 461–62 (1940).—Zinc oxide improves the chemical and physical properties of glass and enamel. It is manufactured from metallic zinc and is very pure with little foreign substance; 0.2% lead is harmless, but larger amounts may cause yellow coloring. The zinc sulfate content is low (0.2%). In the glass industry, zinc oxide is used to make optical glasses with special properties; in the manufacture of apparatus glass, it replaces the alkaline earths (calcium oxide and barium oxide) and increases the resistance of these glasses to watery solutions and sudden temperature change. In colored or opacified glasses, it cannot be replaced. The coloring action of some rare earths is often intensified or varied by zinc oxide; the opacifying action of fluorine compounds is promoted by zinc oxide, and the whiteness of the enamel is increased, as is that in the case of opacification with air bubbles. Zinc oxide is an excellent flux and refining agent and can replace boric acid. The zinc silicate formed during glassmaking minimizes the expansion of glass from temperature fluctuations and lowers its tendency to break; it also retards aging or dulling. In the enamel industry, zinc oxide is used as a flux in glazes to replace boric acid; the enamel melts at lower temperatures, is free from nodules or flaws when cool, and has sufficient chemical and mechanical resistance. Zinc oxide aids the opacifying of enamels; it makes them more ductile and prevents crazing. See *Ceram. Abs.*, **19** [4] 91 (1940). M.V.C.

PATENTS

Absorptive glass. R. A. MILLER (Pittsburgh Plate Glass Co.). U. S. 2,223,118, Nov. 26, 1940 (March 25, 1938).—A laminated glass unit having capacity to absorb ultraviolet rays and X rays.

Air-tight envelopes of which ceramic materials form part. GENERAL ELECTRIC CO., LTD., J. R. LAIT, AND J. H. PARTRIDGE. Brit. 528,229, Nov. 6, 1940 (May 1, 1939).

Apparatus for:

Bending glass sheets. WILLIAM OWEN (Pittsburgh Plate Glass Co.). U. S. 2,223,123, Nov. 26, 1940 (April 8, 1938).

Making articles such as glassware. D. I. DU BOIS (Armstrong Cork Co.). U. S. 2,224,767, Dec. 10, 1940 (July 7, 1936).

Running molten glass, etc., into molds. J. ROBINSON. Fr. 835,697, March 24, 1938. D.A.B.

Securing local illumination. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 829,960, March 12, 1937. D.A.B.

Tempering glass. AMERICAN SECURIT CO. Fr. 842,502, Aug. 25, 1938. D.A.B.

Apparatus and process for:

Applying a coating on a glass tube. COMPAGNIE DES LAMPES. Fr. 830,541, Dec. 8, 1937. D.A.B.

Feeding glass into machines for manufacturing bottles, etc. J. T. WOOD. Fr. 842,271, Aug. 18, 1938. D.A.B.

Manufacturing sealed glass objects. CORNING GLASS WORKS. Fr. 843,143, Sept. 7, 1938. D.A.B.

Manufacturing sheet glass. AMERICAN WINDOW GLASS CO. Fr. 842,279 to 842,282, Aug. 18, 1938. D.A.B.

Manufacturing stopcock holes starting with glass tube. KIMBLE GLASS CO. Fr. 844,311, Oct. 4, 1938. D.A.B.

Winding glass fibers, thread, wicks, ribbons, etc., at high speeds. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 842,764, Aug. 29, 1938. D.A.B.

Automatic machine for manufacturing bottles and flasks. J. TOURRES. Fr. 845,070, April 20, 1938. D.A.B.

Borosilicate glass. H. P. HOOD AND M. E. NORDBERG (Corning Glass Works). U. S. 2,221,709, Nov. 12, 1940 (Jan. 29, 1938).—A glass contains silica, boric oxide, and alkali, the silica being over 94%, the boric oxide being under 6%, and the alkali being under 0.25%.

Building block. L. W. MULFORD. U. S. 2,221,649, Nov. 12, 1940 (Aug. 5, 1939).

Coating glass sheets. C. S. SHOEMAKER (American Window Glass Co.). U. S. 2,224,236, Dec. 10, 1940 (April 26, 1939).

Coatings for insulators made of glass fibers and mineral wool. I. G. FARBENIND. A.-G. Fr. 845,489, Oct. 31, 1938. D.A.B.

Constructing wall linings for furnaces for fusing glass. HARTFORD-EMPIRE CO. Fr. 844,970, Oct. 20, 1938. D.A.B.

Construction element made of glass. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 836,426, Sept. 29, 1937. D.A.B.

Cream-separating milk bottle. R. W. MCALISTER. U. S. 2,222,511, Nov. 19, 1940 (Nov. 21, 1939).

Evacuating a vessel and making a vitreous seal. D. V. EDWARDS (Electrons, Inc.). U. S. 2,223,031, Nov. 26, 1940 (Dec. 19, 1935; Aug. 25, 1939).

Gas-tight joints between metallic and ceramic insulating bodies. R. BOSCH GES. Brit. 527,580, Oct. 23, 1940 (April 27, 1938).

Glass brick and method and apparatus for making. W. S. RENDALL (Crown Cork & Seal Co., Inc.). U. S. 2,224,488, Dec. 10, 1940 (Oct. 29, 1936).

Glass composition. H. H. BLAU (Corning Glass Works). U. S. 2,224,469, Dec. 10, 1940 (Feb. 28, 1938).—A light-diffusing nonborosilicate glass containing at least 65% of silica and also alkali oxide, alumina, and at least 3% of analytically determined fluorine, being substantially free from second-group oxides, the ratio of alkali oxides to alumina being 1.85 to 3.5.

Glassmelting tank. C. C. KING. U. S. 2,222,816, Nov. 26, 1940 (March 10, 1939).

Glass-to-metal seal. W. J. GEIGER AND WILSON DAVIDSON (General Electric Co.). U. S. 2,221,868, Nov. 19, 1940 (Sept. 23, 1938).

Glassworking machines. CORNING GLASS WORKS. Brit. 527,692, Oct. 23, 1940 (March 19, 1938).

Heating ovens, particularly those for hardening glass

plates. GLACERIES RÉUNIES SOC. ANON. Brit. 527,661 and 527,662, Oct. 23, 1940 (April 27, 1938).

High silica glass composition. W. C. TAYLOR (Corning Glass Works). U. S. 2,224,493, Dec. 10, 1940 (March 26, 1938).—A transparent soda-alumina-silicate glass containing not over 85% SiO_2, the sum of the percentages of silica, soda, and alumina comprising at least 97% of the glass and being in the proportions 80 to 85% SiO_2, 10 to 15% Na_2O, and 2.5 to 7.5% Al_2O_3, and containing calcium and showing by analysis the presence of fluorine.

Insulating element consisting of glass fibers or glass wool. COMPAGNIES RÉUNIES DES GLACES ET VERRES SPÉCIAUX DU NORD DE LA FRANCE. Fr. 844,457, April 5, 1938. D.A.B.

Lehr drive for sheet-glass machines. WILLIAM OWEN (Pittsburgh Plate Glass Co.). U. S. 2,223,122, Nov. 26, 1940 (Sept. 29, 1937).

Lens-drilling machine. A. E. MAYNARD (American Optical Co.). U. S. 2,222,538, Nov. 19, 1940 (April 25, 1938).

Lens-edging machine. E. M. LONG (Shuron Optical Co., Inc.). U. S. 2,221,737, Nov. 12, 1940 (Oct. 2, 1937; Aug. 15, 1938).

Machine for grinding or polishing lenses. D. TAYLOR. Brit. 528,724, Nov. 20, 1940 (May 13, 1939).

Machine for producing bases for glass vessels from tubular disk or plate. KIMBLE GLASS CO. Fr. 844,310, Oct. 4, 1938. D.A.B.

Machines for the production of tablet glasses, ampoules, etc. J. DICHTER. Brit. 528,031, Oct. 30, 1940 (Aug. 25, 1939); addition to 467,282.

Making mineral wool. C. F. RAMSEYER. U. S. 2,223,047, Nov. 26, 1940 (March 9, 1936).

Manufacture of electric lamps or discharge devices having vitreous foot-tubes closing vitreous envelopes. GENERAL ELECTRIC CO., LTD. Brit. 528,291, Nov. 6, 1940 (Nov. 3, 1938).

Manufacture of glass ampoules. HARRY RICHTER (Kimble Glass Co.). U. S. 2,224,486, Dec. 10, 1940 (Sept. 14, 1937).

Manufacture of laminated glass. F. L. BISHOP, R. H. DU BOIS, AND PATRICK FINNEGAN (American Window Glass Co.). U. S. 2,221,367, Nov. 12, 1940 (May 6, 1933).

Manufacturing glass articles having the shape of goblets. V. HRDINA. Fr. 842,950, Sept. 3, 1938. D.A.B.

Manufacturing porous fibrous glass. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 842,585, Aug. 25, 1938. D.A.B.

Manufacturing a shield consisting of glass fibers for electric accumulators, etc. COMPAGNIES RÉUNIES DES GLACES ET VERRES SPÉCIAUX DU NORD DE LA FRANCE. Fr. 844,212, March 31, 1938. D.A.B.

Material made of sponge glass for construction purposes. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 844,825, April 14, 1938. D.A.B.

Metal-to-glass seals. STANDARD TELEPHONES & CABLES, LTD. Brit. 528,699, Nov. 20, 1940 (July 2, 1938).

Method and apparatus for bending and casehardening glass sheets. WILLIAM OWEN (Pittsburgh Plate Glass Co.). U. S. 2,223,124, Nov. 26, 1940 (July 19, 1938).

Method and apparatus for producing mineral wool. H. F. VIEWEG, H. E. HOLCOMB, G. T. PEARCE, AND H. T. COSS (Johns-Manville Corp.). U. S. 2,221,011, Nov. 12, 1940 (Sept. 3, 1937).

Mirror. COMPAGNIES RÉUNIES DES GLACES ET VERRES SPÉCIAUX DU NORD DE LA FRANCE. Fr. 842,424, Feb. 16, 1938. D.A.B.

Molten inorganic salt baths for thermal treatment. PILKINGTON BROS., LTD. (Corning Glass Works). Brit. 528,135, Nov. 6, 1940 (April 27, 1939).

Optical grinding machine. A.-G. VORM. SEIDEL & NAUMANN. Fr. 841,512, Aug. 1, 1938. D.A.B.

Perforated plate or receptacle for fused glass, etc. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 843,232, Sept. 9, 1938. D.A.B.

Process for the manufacture of selenium-containing ruby glass. HANS LÖFFLER (Deutsche Gold und Silber Scheideanstalt, vorm. Roessler). U. S. 2,224,791, Dec. 10, 1940 (June 7, 1937).—In a process for manufacturing selenium-containing ruby glasses which contain cadmium in addition to selenium, wherein the ruby color is developed by a reheating subsequent to the melting and cooling of the glass batch, the improvement comprises incorporating in the batch from which the glasses are prepared an agent selected from the group consisting of alkali-metal sulfides, alkali-metal thiocyanates, and zinc thiocyanate, whereby the formation of color in the reheating step is accelerated.

Producing phosphorescent objects having refractive surfaces. J. A. CHIRAT AND J. MOTTE. Fr. 843,040, Feb. 28, 1938. D.A.B.

Protecting the edges of glass sheets or plates. COMPAGNIES RÉUNIES DES GLACES ET VERRES SPÉCIAUX DU NORD DE LA FRANCE. Fr. 843,035, Feb. 26, 1938. D.A.B.

Suction cup glass-feeding mechanism and method. R. W. CANFIELD (Hartford-Empire Co.). U. S. 2,224,759, Dec. 10, 1940 (Sept. 12, 1936).

Tempering glass. GILT EDGE SAFETY GLASS, LTD. Fr. 842,591, Aug. 25, 1938. D.A.B.

Tinted glass. CORNING GLASS WORKS. Brit. 527,757, Oct. 30, 1940 (June 25, 1938).

Structural Clay Products

Comparison of effectiveness of header courses and metal ties in brick walls. A. L. MILLER AND H. L. BUSHNELL. *Bull. Amer. Ceram. Soc.*, **19** [12] 474–77 (1940).—4 figures.

Development in brick pavements. W. H. CULLIMORE. *Dependable Highways*, No. 168, pp. 12–15 (1940).—Outstanding improvements in brick paving during the past decade are (1) manufacture of dealred brick, (2) manufacture of vertical fiber lug brick with wire cut wearing surface, (3) use of mastic bedding courses, (4) rolling on boards, and (5) removal of the bituminous filler from brick surfaces by the use of separating agents. These improvements are discussed in detail. Illustrated. P.S.D.

Manufacture of lightweight products. HARRY D. FOSTER. *Bull. Amer. Ceram. Soc.*, **19** [12] 468–73 (1940).—76 references.

Recent developments of reinforced brick pavement. ANON. *Dependable Highways*, No. 168, pp. 10–11 (1940).—The history and construction details of reinforcement applied to brick pavement projects in Illinois are given. Illustrated. P.S.D.

Vibrated monolithic pavements in Ohio. ANON. *Dependable Highways*, No. 168, pp. 6–7 (1940).—Illustrated. See *Ceram. Abs.*, **19** [10] 235 (1940). P.S.D.

West Road grade separation brick pavement in Trenton, Mich. F. S. ROSER. *Proc. Nat. Paving Brick Assn.*, **1940**, 58–63; *Dependable Highways*, No. 168, pp. 3–5 (1940).—Details of construction are given. Illustrated. P.S.D.

PATENTS

Machine for producing ornaments on brick. L. BENTLEY AND E. GARFORTH. Fr. 843,291, Sept. 12, 1938. D.A.B.

Paving brick and vitreous lining plates. MAISON DÉSIRÉ HUART & FILS. Fr. 844,193, March 30, 1938. D.A.B.

Refractories

Action of alkalis on refractory materials: XII, Effect of heat on refractory materials impregnated with sodium carbonate and sodium hydroxide. F. H. CLEWS, H. M. RICHARDSON, AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 49–55 (Oct., 1939).—Test pieces were impregnated with sodium carbonate and sodium hydroxide solutions, dried, and heated to 1000°C. for 5 hr.; the procedure was repeated a number of times. Under these conditions expansion of fire-clay and silica test pieces occurs, but examination has shown certain marked contrasts with the expansion previously noted in connection with the action of sodium and potassium chloride vapor. The expansion with sodium carbonate and sodium hydroxide is ascribed to a more or less uniform distension of the refractory due to the evolution of gas (carbon dioxide from the carbonate and steam from the hydroxide) in a material rendered deformable by chemical reaction with the sodium compounds. **XIII, Effect of potassium chloride vapor on the transverse strength at 1000°C.** *Ibid.*, pp. 56–59.—In a previous report similar transverse strength determinations were made at room temperature. The potassium chloride causes a weakening of all the materials tested. Fire-clay materials are weakened but are not appreciably softened, whereas silica and siliceous products are markedly softened. Differences in behavior are ascribed to the larger extent of liquefaction caused by reaction of the potassium chloride with the silica and siliceous products compared with that occurring on reaction with fire-clay materials. For Part XI see *Ceram. Abs.*, **19** [2] 46 (1940); for Parts IV and V see *ibid.*, **20** [1] 17 (1941). P.S.D.

Action of slags on refractory materials: III, Action of a series of lime-alumina-silica-iron oxide slags on an aluminous firebrick. W. HUGILL, J. VYSE, AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 76–83 (Oct., 1939).—The report deals with the action of a series of four-component slags on a particular type of alumina-silica refractory. Three different test methods were used: (1) cone fusion of powdered slag-brick mixtures; (2) corrosion and penetration of slag cylinders melted on the surface of test brick; and (3) erosion due to injecting powdered slag into a flame impinging on the test brick. Petrographic studies of reaction products were included. "Iron"-free anorthite can crystallize from the reaction products of firebrick and slags containing considerable iron oxide, and the lowest melting composition, at about 1080°C., corresponds approximately to the eutectic of anorthite, magnetite, and mullite. For Part II see *Ceram. Abs.*, **19** [2] 46 (1940). P.S.D.

Action of steam and sulfur dioxide on refractory materials: I, Action on fire clay at 1200°C. L. R. BARRETT, N. E. DOBBINS, AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 33–45 (Oct., 1939).—A fire clay-grog mixture was heated at 1200°C. for periods up to 222 hr. in atmospheres of steam, oxygen, sulfur dioxide, and mixtures of these gases. Changes in physical properties were small. Shrinkage and reduction in porosity were greater after heating in steam and in sulfur dioxide than after heating in oxygen, sulfur dioxide and oxygen, and dissociated sulfuric acid, where the shrinkages were similar. Specimens heated in steam and in sulfur dioxide were darkened in color and contained ferrous iron compounds. Extra shrinkage and color changes appear to be caused by the absence of free oxygen in these atmospheres. Reheating increased the modulus of rupture in each case. The presence of steam aided vitrification and increased strength, while the presence of sulfur trioxide nullified to some extent the effect of reheating. This may be ascribed to the loss of bond, since notable proportions of lime and magnesia were removed as sulfates on leaching with water. The atmosphere in which cooling took place affected the amount of the soluble sulfates formed, the amount being least when the atmosphere was inert. P.S.D.

Basic refractories. HARLEY C. LEE. *Metal Progress*, **38** [4] 585, 600 (1940).—L. discusses the trends in the development and application of basic refractories such as dolomite, magnesia, and chrome-magnesia brick. J.J.H.

Behavior of sillimanite mixes on being pressed: III, Further experiments on the variations in texture at different positions in the pressed block. F. H. CLEWS, W. F. FORD, AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 68–76 (Oct., 1939).—Experiments were made on the alteration of grain-size ratios and the variation in permeability at different positions and depths in pressed blocks. In general, there is a decrease in the degree of compactness as the distance from the face receiving the pressure increases. Evidence is presented to show that additional crushing may also occur in contact with the metal surfaces of the mold, e.g., at the walls and base. Certain anomalies in results given in previous reports may be explained by these observations. For Part II see *Ceram. Abs.*, **18** [8] 211 (1939). P.S.D.

Blast-furnace construction and operation. W. A. HAVEN. *Metal Progress*, **38** [4] 583 (1940).—A brief review of improvements during the past year is given. J.J.H.

Causes of irregular destruction of arches of open-hearth furnaces. V. V. REVENKO. *Teoriya & Praki. Met.*, **11** [1] 34–35 (1939); abstracted in *Chem. Zentr.*, **1939, II**, 351.—The irregular destruction of refractory linings of open-hearth furnaces is caused by the fact that strong heat flows subject parts of the masonry to very high temperatures; hence, they are liable to greater destruction than parts subjected to lower temperatures. M.V.C.

Effect of hydrocarbon gases on refractory materials: VII, Change in composition of coal gas when passed over refractory materials at 800°C. E. ROWDEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 45–49 (Oct., 1939).—Dry coal gas direct from the mains does not cause the disintegration of certain types of firebrick at about 800°C., but town gas from which carbon dioxide has been removed can disrupt similar specimens in a relatively short period. The changes in composition of coal gas during passage over fire-clay specimens susceptible to disintegration were investigated. Dry coal gas freed from carbon dioxide and oxygen and dry coal gas direct from the mains were used in the experiments. In the first case, disintegration of certain specimens occurred in 18 to 40 hr. accompanied by an increase in the hydrogen content and a decrease in the methane content of the gas. Results from the second experiment were in marked contrast: the percentages of methane and carbon monoxide increased slightly and the percentage of hydrogen decreased slightly on passing through the reaction tube. No disintegration of the specimens occurred during 200 hr. of treatment at 800°C. Methane is apparently the constituent in town gas which is responsible for disruption, producing disintegration by the growth of carbon around activated "iron spots" by the reaction $CH_4 \rightarrow C$ plus $2H_2$. For Part VI see *Ceram. Abs.*, **18** [8] 212 (1939). P.S.D.

Factors affecting thermal conductivity of nonmetallic materials. J. B. AUSTIN. *Brick & Clay Record*, **94** [3] 42–44 (1939).—The factors believed to influence thermal conductivity are chemical composition, physical texture, temperature, pressure, and heat flow. Results show that of these variables the most important are (1) total void space, (2) chemical composition, (3) temperature of service, and (4) time and temperature of firing. Physical texture, in particular total void space, has the greatest influence. The effect of porosity and chemical composition on thermal conductivity is discussed. J.J.H.

Firebrick and bonding mortars for steam-boiler furnaces. E. H. WHITNEY. *Nat. Engr.*, **44** [5] 348–52 (1940).—W. discusses spalling, slagging, and abrasion with respect to their effect upon the life of firebrick and boiler settings. Firebrick manufacturing processes are described briefly, and their effect upon brick life is considered. The

properties of several types of brick mortar and cement are presented, and their application for specific operating conditions are discussed. Illustrated. F.G.H.

Growth of carbon in the fire-clay joints at top of an intermittent vertical chamber setting. P. C. GARDINER. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 105–15 (Oct., 1939).—G. describes conditions leading to the formation of carbon in the joints of the two top courses of firebrick which caused the irregular rising of the tops of the setting. He concludes that the deposition was caused by the decomposition of hydrocarbons in the joints and that there was a slight gas pressure in the top of the chambers which caused tar and gas to penetrate therein. Initial joint opening is accounted for by variations in temperature in charging and discharging. In some joints substantial deposits of iron oxide were associated with the carbon. These iron deposits probably came from the coal ash. G. strongly recommends that careful attention be given to the control of pressure and vacuum in the chambers. Alterations in the gas off-take system to overcome the carbon deposition are described. P.S.D.

High-porosity sillimanite brick: II, Properties of fired sillimanite mixes containing paper pulp. F. H. CLEWS, N. E. DOBBINS, AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 97–102 (Oct., 1939).—It was thought that the fibrous nature of paper pulp might be utilized to advantage in imparting the texture required for low conductivity at high temperatures. Experimental products showed promise from the viewpoints of required texture and stability under load at 1350°C. but suffered from a tendency to crack on firing and possessed considerable drying shrinkage. Shrinkage and cracking tendencies were reduced by including porous grog in the mixes but at some sacrifice of stability under load. For Part I see *Ceram. Abs.*, **17** [2] 71 (1938). P.S.D.

Hot patching of refractories by blowpipe spray welding. C. H. S. TUPHOLME. *Ind. Eng. Chem., News Ed.*, **17** [12] 426–27 (1939); see *Ceram. Abs.*, **19** [6] 141 (1940). F.G.H.

Insulating brick and superrefractories. S. N. DUGUID. *Steam Engr.*, **9**, 288–90 (1940).—The properties required in insulating brick in general and in those intended only for use behind a dense refractory wall are given. The physical characteristics of diatomaceous earth and test data on two brands of brick made therefrom are presented. Special refractories described are fused alumina, silicon carbide, and sillimanite. L.R.B.

Jointing cements: IX, Effect of additions of some electrolytes on the workability of clay-grog mixtures. F. H. CLEWS, H. M. RICHARDSON, AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 59–65 (Oct., 1939).—Measurements of water-retaining capacity and tendency to spread under vibration were made on several mixtures of bond clays and grogs. Results indicate that the working properties of cements may be appreciably altered and, in some cases, improved by the addition of electrolytes. **X, Stability of cement mixes at 1300°C. containing uncalcined kyanite.** *Ibid.*, pp. 65–76.—The apparatus and procedure described in previous reports were used. Results indicate that uncalcined kyanite, added in suitable amount to clay-sillimanite (calcined kyanite) cements, is beneficial in counteracting the contractile tendency of the clay bond at high temperatures. For Part VIII see *Ceram. Abs.*, **18** [8] 213 (1939). P.S.D.

Manufacture of machine tool castings. J. BLAKISTON. *Engineer*, **166** [4306] 102–103 (1938).—B. discusses the Brackelsburg furnace as a rotary melting unit for machine tool castings. The monolithic lining for rotary furnaces has presented difficulties to users of this type of melting unit. The general practice with furnaces of 10-ton capacity has been to reline the furnace entirely after 100 to 150 heats. The following method has been found satisfactory for lining this type of furnace when operating intermittently: the casing is first lined with $4^1/_2$ in. of common firebrick to form a backing, and the furnace is then lined with first-class ganister by ramming round a former. The higher the silica content of the lining material, the greater is the contraction and expansion range, rendering the lining more friable under mechanical shock. Ganister with 86% silica may not be so refractory for extremely high temperatures, but it can be patched more easily; a furnace lined with it can be maintained similar to a cupola. A 10-ton furnace gave over 300 heats without a major reline. This type of lining is "active," meaning that the metal does not have the tendency to stick to it and become oxidized. An air-furnace bottom must be made up with silver sand after 12 or more heats to keep it active. To maintain this state in the rotary furnace, about 2 cwt. of sea sand is thrown in after each heat when the slag has been drained out, and the furnace is kept revolving to distribute it evenly. This sand frits to the lining. F.G.H.

Manufacture of refractory insulating brick. FELIX SINGER. *Brit. Clayworker*, **49** [580] 103–105 (1940).—The following general indications may be found useful: (1) The process employing combustible material permits the manufacture of refractory brick and siliceous refractory brick of a specific gravity of 0.75 or above. In some cases it has been possible to make brick containing 62% alumina. Porous silica brick have been unsatisfactory in use. The process is particularly suitable for making lightweight firebrick of medium quality. (2) The sublimation process, like the method using combustibles, yields products with specific gravities usually exceeding 0.75. The important technical properties of these brick are better than those of brick made by the process using combustibles. If it is possible to regenerate and purify the sublimating substances, the cost of producing these brick is very low. (3) When using porous lightweight grog, it is difficult to obtain lightweight brick having a specific gravity of less than 1.0, but if this process is combined with the use of combustible or sublimating material, products can be obtained which, while more expensive, are more accurate in size and better in quality than brick obtained by the exclusive use of sublimating or combustible matter. (4) The gas-developing process yields porous brick of any desired silica or alumina content which have low specific gravity, great strength, and an excellent insulating power. Special machinery is required for preparing the raw materials, as well as a large number of molds and a special drying tunnel. (5) The use of the foam process requires more expensive equipment than the gas-development process. See *Ceram. Abs.*, **20** [1] 18 (1941). R.A.H.

Orthosilicates of the alkaline earths with special reference to their uses in the refractory field. GILBERT E. SEIL AND STAFF. *Jour. Amer. Ceram. Soc.*, **24** [1] 1–19 (1941).—17 tables, 44 figures. See "Bibliography...," *Ceram. Abs.*, **19** [11] 273–93 (1940). **Discussion.** HARLEY C. LEE. *Jour. Amer. Ceram. Soc.*, **24** [1] 20–21 (1941).—10 references. MAX Y. SEATON. *Ibid.*, pp. 21–22.

Rational composition of the mix for blast-furnace tapholes. G. I. LUK'YANETS AND M. I. LUK'YANETS. *Teoriya & Prakt. Met.*, **11** [4–5] 21–24 (1939); abstracted in *Chem. Zentr.*, **1939, II**, 4306.—The lining of tapholes of blast furnaces is often prepared from local raw materials which are prematurely destroyed by slag. Such a mix may contain up to 2.5% Fe_2O_3. A refractory and slag-resistant mix has been developed which consists of coal tar pitch, coal, grog powder, and refractory clay. Its chemical analysis is as follows: 44 to 45.3 SiO_2, 15.08 to 15.57 Al_2O_3, 0.43 to 0.92 Fe_2O_3, 0.92 to 1.24 CaO, 0.51 to 0.58 MgO, and 0.46 to 1.26% H_2O; loss on ignition 35 to 37.1%. The mix showed good resistance to highly aggressive basic slag. The mix without grog was also satisfactory. M.V.C.

Refining steel in the high-frequency furnace. VICTOR STOBIE. *Engineer*, **164** [4277] 751–52 (1937).—Refractory requirements are briefly discussed. Illustrated. F.G.H.

Refractories for gas- and coke-burning appliances. L. R. BARRETT AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 10–33 (Oct., 1939).—Experiences and information

relative to refractories used in town gas- and coke-burning appliances have been collected and supplemented by a literature review. Service requirements imposed on refractory firebacks for gas and coke fires and the extent to which existing materials fall short of desired standards lead to the conclusion that improvement of materials is possible. Special features of insulating firebrick are discussed. Calculations and experiences are quoted to show economy of fuel and time associated with their use. Limitations of insulating refractories suggest that a composite brick should be developed which would possess the durability of a dense firebrick under adverse conditions of temperature fluctuation, flying slag particles, and mechanical abuse and at the same time possess the heat-conserving properties of porous insulating brick. Experiences with the use of thin glaze coatings and cement coatings on the hot face of insulating firebrick and data on the radiation reflectance of refractories are given. Silicon carbide has almost all of the properties required of a high-temperature heat conductor, but, because of the swelling and oxidation which sometimes occur at certain temperatures, in some cases its use has been discontinued in favor of fused alumina. Conditions surrounding the use of refractories in some town gas-fired pottery and steel-heating installations are described. P.S.D.

Refractories for the modern boiler furnace. S. L. DAVIS. *Nat. Engr.*, **44** [4] 258–61, 265 (1940).—D. describes the fundamental properties of fire-clay refractories and briefly discusses the effects of operating conditions of boiler furnaces of varying capacities upon refractories. Illustrated. F.G.H.

Refractory materials. S. N. DUGUID. *Steam Engr.*, **9**, 255–57 (1940).—The methods adopted in Great Britain for the manufacture of fire-clay brick and silica brick are described, and statements regarding firing temperatures are given. Test data for brick with more than 96% silica and ganister brick are given with notes on their correct use. L.R.B.

Relation between the viscosity of slags and their attack on refractory materials. J. R. RAIT AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 83–96 (Oct., 1939).—The literature on the subject is reviewed. It is concluded that future studies of slagging require investigation into the relationship between the viscosity of slags and their composition and temperature, the solubility of refractory materials in the slags, the rates of diffusion of the liquids formed, and the measurement of erosion under controlled conditions. P.S.D.

Research and refractory materials, 1938. F. H. CLEWS AND A. T. GREEN. *Rept. Refrac. Materials Joint Comm., 30th Rept., Inst. Gas Engrs. Commun.*, No. 218, pp. 102–104 (Oct., 1939).—G. presents a short review of researches and reports of interest to gas engineers with a list of researches of the British Refractories Research Assn. P.S.D.

Silica in coke-oven practice. E. ALTON. *Coke & Smokeless Fuel Age*, **2**, 116–18, 131–34 (1940).—The physics and chemistry of silica are discussed for the particular benefit of those engaged in the coke-oven industry. The topics discussed include (1) effect of fine-grinding and fluxes on inversion in the firing of silica brick, (2) technological importance of the Fenner diagram, (3) volume relationships of the phases of silica, (4) use of specific-gravity determinations in conjunction with microscopic examination and measurement of reversible thermal expansion to determine the nature and relative proportions of the three chief forms of silica present in a brick, (5) porosity and permeability of silica coke-oven brick, (6) heat transfer as influenced by size of pores, and (7) storage of silica brick. L.R.B.

Special refractories. GILBERT E. SEIL. *Metal Progress*, **38** [4] 583–85 (1940).—Dolomite, olivine, magnesia, and magnesia-chrome refractories are discussed briefly. J.J.H.

Stress-relieving furnace for welded structures. L. G. A. LEONARD. *Metallurgia*, **22** [131] 137–38 (1940).—Refractory construction of both walls and roof is described in detail. Illustrated. F.G.H.

Superrefractories and the measurement of high temperatures. S. N. DUGUID. *Steam Engr.*, **9**, 330–31 (1940).—The manufacture and properties of magnesite brick are outlined. Zirconia and chrome brick are referred to. The construction, method of operation, and use of radiation pyrometers are described in connection with furnace operation and the measurement of the temperature of molten metals in the open. L.R.B.

PATENTS

Alumina extraction. J. C. SÉAILLES AND W. R. DYCKERHOFF. Fr. 840,689, July 15, 1938.—Materials high in silica content are employed such as earthen material, artificial silicates, aluminum silicate, or calcareous schist. D.A.B.

Cast refractory with adequate porosity. BUNPEI YOSHIKI (Corning Glass Works). U. S. 2,224,498, Dec. 10, 1940 (Sept. 9, 1937).—A cast refractory substantially consists of crystals of spinel and forsterite and analytically contains between 40 and 20% of alumina and between 20 and 30% of silica, the remainder being magnesia.

Chromite refractory materials. G. E. SEIL. Brit. 527,470, Oct. 23, 1940 (April 13, 1939).

Coatings for refractory brick. E. J. LAVINO & Co. Fr. 838,343, May 23, 1938. D.A.B.

Electric furnace roof construction. M. K. SMITH (Latrobe Electric Steel Co.). U. S. 2,222,004, Nov. 19, 1940 (Aug. 3, 1939).

Furnace wall. F. B. BIGELOW (Bigelow-Liptak Corp.). U. S. 2,223,400, Dec. 3, 1940 (May 29, 1939). U. S. 2,223,401, Dec. 3, 1940 (Aug. 21, 1939).

Graphite refractory article. R. M. SHREMP (Lava Crucible Co. of Pittsburgh). U. S. 2,222,184, Nov. 19, 1940 (Sept. 19, 1939).—Refractory articles comprise graphite, residual carbon bond, and an oxygen compound of manganese, the articles having in consequence of the oxygen compound of manganese a self-healing protective glaze.

Making lightweight refractory brick. C. S. MATHENY (National Fireproofing Corp.). U. S. 2,224,450, Dec. 10, 1940 (July 15, 1937).—The method of making lightweight refractory insulating brick comprises mixing the batch material of clay with 1 to 50% shredded or comminuted paper, tempering the batch in a wet state to produce a knurly and fibrous structure, molding the batch to the desired shape, and subjecting it to a firing temperature in a kiln to burn out the paper.

Manufacture of crystalline magnesium hydroxide and its use in the production of refractory products. H. H. CHESNY. Fr. 827,065, Sept. 23, 1937. D.A.B.

Manufacture of refractory articles. H. E. WHITE (Lava Crucible Co. of Pittsburgh). U. S. 2,222,188, Nov. 19, 1940 (Aug. 8, 1938).—An emulsion adapted for use in making graphite and like refractory articles containing residual carbon bond comprises a stable emulsion of refractory ceramic material which does not swell in water and when dry is of a slippery, unctuous nature, at least the major proportion of which is subdivided to not over about 20-micron particle size, a liquid which is a nonsolvent for the ceramic material, and a partially volatile resinous binder which provides carbon residue on heating.

Manufacturing aluminates. I. G. FARBENIND. A.-G. Fr. 839,961, June 29, 1938. D.A.B.

MgO and $MgCO_3$ from dolomite and similar materials. O. ORLANDI. Fr. 845,090, April 22, 1938. D.A.B.

Producing refractory blocks. DORTMUND-HOERDER HÜTTENVEREIN A.-G. Fr. 839,489, June 18, 1938. D.A.B.

Refractory brickwork for use in furnaces, kilns, etc. H. H. CHESNY. Brit. 527,710, Oct. 30, 1940 (April 11, 1939).

Refractory material. V. M. GOLDSCHMIDT. Fr. 842,763, Aug. 29, 1938. D.A.B.

Zircon refractories and method of making. TITANIUM ALLOY MFG. CO. Brit. 528,845, Nov. 20, 1940 (Feb. 10, 1938).

Terra Cotta

Factors to consider when making glazed ware: I. JOHN H. GRADY. *Brick & Clay Record*, **94** [2] 16–18 (1939).—Experiments have indicated that no two clays possess the same ability to receive a glaze or have the same coefficient of expansion. It is necessary to fit a glaze individually to every body. Both the fritted and the raw glazes must be designed for the individual body on which they are to be applied. A properly designed raw glaze is far superior to many of the fritted glazes now used by the manufacturers of heavy clay products. Glazes of typical composition and maturing ranges are classified according to type, e.g., lead, leadless, modified Bristol, Bristol, and porcelain. The type to be used on a particular body depends somewhat on the maturing range of the body. The cheapest way to produce glazed ware is to use a glaze designed to have a maturing range similar to that of the body. By applying the glaze on the raw body and maturing both the body and the glaze at the same time the second firing is eliminated. The object of fritting is to complete as many of the chemical reactions as possible before the glaze is applied to the body. When a glaze is applied on a bisque body of low absorption, the water content of the glaze must be decreased to prevent running of the glaze on application. It is customary to add a small quantity of a flocculating agent to the glaze before it is milled. This can be adjusted to cause an almost instantaneous setting of the glaze as it is applied to the ware, even though the ware is very nonabsorbent. The same means is used to decrease the number of glaze applications necessary to produce a coating of the desired opacity. A glaze should be applied with sufficient thickness so that any increased application of material will cause no apparent color change. The opacity of the glaze has then masked the body. Glazes which are applied too thick generally part, peel, or wrinkle. Their surface tensions seem to increase as evidenced by a parting and balling up of the glaze coat. **II.** *Ibid.*, [3] 27–28.—Old style granite and speckled finishes have given way to the warm and harmonious mottled glazed coatings. These liquid coating materials are applied in the shape of drops or slugs. The color combinations which can be produced in this manner are unlimited. Mottle finishes are made by spotting the ware with two or more slips and glazes simultaneously. In spraying several glazes simultaneously, considerable trouble has been experienced in maintaining a constant ratio of the colors being applied. If this ratio is not maintained, the resulting mottle finish will differ in color from the standard. In handling coating material, three distinct factors are found which influence the spraying operation. These are weight per unit volume, apparent viscosity (as measured by a hydrometer), and flowability. **III.** *Ibid.*, [4] 46–48.—The necessity of uniform temperature distribution throughout the ware setting is of prime importance. Another important factor is the need of a surplus of air beyond that actually required for combustion. G. describes and discusses the types of firing and the fuels used in firing glazed ware. Almost any fuel which burns without a solid residue may be used for direct-firing glazed ware provided that the fuel is burned without the setting spaces of the kiln. The effect of sulfur scum is also discussed. J.J.H.

Peeling and scumming problem in red roofing material. COLIN PRESSWOOD. *Trans. Brit. Ceram. Soc.*, **39** [9] 259–65 (1940); *Brit. Clayworker*, **49** [580] 110–12 (1940).—Using the ratio of surface to volume in the drying of laboratory prepared clay briquettes, P. proved that surface scumming was due to the drying of ware during manufacture. This was eliminated by the use of barium carbonate and by better mixing of clays. R.A.H.

PATENT

Tile cutter. G. H. MÉTAFIOT. Fr. 835,611, March 23, 1938. D.A.B.

Whiteware

Experimental data on application of a synthetic organic plasticizing agent. F. F. OGDEN. *Bull. Amer. Ceram. Soc.*, **19** [12] 465–67 (1940).—2 figures.

Testing specifications for ceramic electrical insulating materials. TECHNICAL COMMITTEE OF THE ASSN. OF GERMAN ELECTRICAL PORCELAIN MANUFACTURERS. *Keram. Rundschau*, **48** [4] 27–30; [5] 38–41; [7] 56–59; [10] 88–89 (1940); abstracted in *Electrician*, **125** [3250] 137–38 (1940).—It has been the practice on the Continent, particularly in Germany, for electrical porcelain manufacturers to publish elaborate data tables of the physical and electrical characteristics of their products. Regulations standardizing the methods of determining these characteristics have been issued so that in future the data tables published by the various manufacturers will be directly comparable. The properties specified and brief descriptions of the methods of making the measurements are given. (*1*) *Porosity:* Pieces of porcelain broken from the insulators to be tested are placed in a thin-walled lead capsule which is filled with an alcoholic solution of fuchsin dye and closed by a rubber stopper. The capsule is then immersed in an oil-filled pressure vessel, and the oil pressure is raised by pump to the required value. The product of the pressure and the time of application shall be at least 1500 atm. hr. with a minimum pressure of 150 atm. The pieces are further broken after the test and should show no penetration of the dye. (*2*) *Water absorption:* A sample of approximately 50 gm. weight is dried out for 3 hr. at 150°C. and cooled in a desiccator over calcium chloride before weighing. The sample is then placed in a vacuum (pressure less than 50 mm. of mercury) for 15 min. before air-free distilled water is admitted to the vessel to completely cover the sample. After 12 hr. the sample is removed, and the surface water is dried off before the sample is weighed again to determine the percentage increase in weight. (*3*) *Density:* This is determined by weighing a regularly shaped piece. (*4*) *Tensile strength:* A dumbbell-shaped specimen is used, the tensile load being applied by two jaws made of steel plate 16 mm. thick. Copper foil is placed between the jaws and the specimen to prevent concentrations of stress. (*5*) *Compressive strength:* A cylindrical specimen 25 mm. long and 25 mm. in diameter with the end faces carefully ground flat and parallel is tested. Cartridge paper is placed on the compression faces as a stress distributor. (*6*) *Bending strength:* The specimens used are rods 120 mm. long, the cross section depending on the method of manufacture. The circular section is used for plastic processes and the oval section for pressing processes. The sample is supported on two rollers 10 mm. in diameter and 100 mm. apart, and the load is applied through a centrally placed third roller. The breaking stress is then calculated by the usual beam formula. (*7*) *Impact strength:* Samples described in 6 are tested between 100-mm. centers in a pendulum-type impact-testing machine. The pendulum has an initial energy of 10 kgm. cm. which is sufficient to cause breakage. The strength is expressed in kgm. cm./cm.^{2} units and is obtained by dividing the energy absorbed from the pendulum in producing fracture by the cross-sectional area of the sample. (*8*) *Hardness:* Hardness is determined by scratching tests and is expressed in terms of Mohs' scale. (*9*) *Linear coefficient of thermal expansion:* This is measured by any of the usual methods and is expressed as a mean value over the range of 20° to 100°C. (*10*) *Specific heat:* This property is determined by a calorimetric method. The sample is heated in a vertical tube surrounded by a steam jacket which is held over a calorimeter, a polished aluminum plate being interposed between the two to reduce the heat transfer. When the specimen has attained a steady temperature, the aluminum

plate is removed and the sample is dropped into the calorimeter. (*11*) *Heat conductivity:* The absolute determination of this quantity is difficult, and it is not considered advisable to specify this as a works test. Heat conductivity can be determined from the temperature conductivity as follows: heat conductivity = temperature conductivity × density × specific heat. (*12*) *Temperature conductivity:* The apparatus for measuring the temperature conductivity consists of a double-walled nickel crucible. The crucible is filled with mercury, and steam is passed through the hollow walls. After a period of 10 min., the porcelain test disk, about 50 mm. in diameter and 10 mm. in thickness, is placed so that it floats on the mercury. A crystal of diphenylamine placed on the upper surface of the disk indicates when the temperature reaches 50°C. The temperature conductivity is then $\frac{d^{1.7}}{t} \times K$ (in cm.²/second), where d = thickness of disk, t = time in seconds until the melting of the crystal, and K = apparatus constant. K is determined by first carrying out the test using a standard glass disk of known conductivity. (*13*) *Resistance to sudden temperature change:* Three cylindrical specimens 25 mm. long and 25 mm. in diameter are placed in a small electric furnace and heated to 100°C. for half an hour. The furnace is then turned into a vertical position to allow the samples to fall into a water bath at 20°C. This test is repeated, the upper temperature being increased 10°C. each time until failure, which usually takes the form of fine surface cracks, occurs. (*14*) *Heat resistance (softening temperature):* This quantity is determined by testing a small cone-shaped specimen alongside standard Seger cones, the temperature being raised so that the time between the softening of two consecutive cones is about 15 min. (*15*) *Resistance to chemical action:* No specification. (*16*) *Puncture strength:* A gradually increasing voltage is applied between the spherical recess and the opposite face of a disk until breakdown occurs at a voltage (V). The breakdown stress is as follows: $g = \frac{V}{d} f$, where d is the minimum thickness and f is a factor which allows for nonuniformity of the electric field. Table I shows how f varies with the thickness (d).

TABLE I

d (mm.)	f
1.0	1.068
1.5	1.102
2.0	1.137
3.0	1.208
4.0	1.283
5.0	1.359

(*17*) *Dielectric constant:* The capacity of standard disks is measured. With the disk for low-frequency high-voltage measurements, the capacitance is measured by bridge methods. With the disk for low-voltage high-frequency measurements, resonance methods are used to determine the capacitance. (*18*) *Temperature coefficient of dielectric constant:* This is to be measured on disks as described in 17. No apparatus or test methods are given. (*19*) *Dielectric losses:* At low frequencies dielectric loss is determined by Schering bridge measurements, the voltage being such as to produce an electric stress of 10 kv./mm. in the material. The test is made under oil. At high frequencies a resonance method is to be used, in which the sample is compared with a loss-free air condenser of equivalent capacitance. (*20*) *Dielectric loss at high temperature:* The measurements are made as described in 19 but at temperatures of 60°, 80°, and 100°C. (*21*) *Insulation resistance—variation with temperature:* The test is made on a disk whose opposite faces are metallized. If the resistance is measured by the application of a. c., an allowance must be made for the capacitance current. In this case silver is a suitable metal for the metallic layer. The resistance may alternatively be measured by the applica ion of a steady voltage, but to reduce electrolytic effects the voltage must be applied only for a short time. Platinum electrodes must be used in this case. The test is carried out at varying temperatures up to 600°C., the sample being heated in an electric furnace. (*22*) *Surface resistivity:* This value is obtained by measuring the current flowing after a direct voltage of 1000 v. has been applied between two line electrodes 100 mm. long and 10 mm. apart, which may consist of graphited or metallized lines on the insulator surface. This quantity is greatly dependent on the atmospheric humidity, and the measurement should be made at 63% relative humidity. (*23*) *Resistance to tracking:* Ceramic materials are not subject to tracking, and no specification is issued. (*24*) *Resistance to arcing:* As ceramic materials contain no combustible constituents, they are unaffected by arcing. A data table shows the properties to be expected in the various classes of electrical porcelain. The most interesting properties are given in Table II (see pp. 50 and 51). H.K.R.

PATENTS

Apparatus for testing concentricity of spark-plug porcelains. C. C. SOPER (Firestone Tire & Rubber Co.). U. S. 2,221,154, Nov. 12, 1940 (Sept. 24, 1938).

Electrical insulating object made of dense ceramic materials possessing a constantly high dielectric. PORZELLANFABRIK KAHLA. Fr. 827,156, Sept. 27, 1937. D.A.B.

High-voltage insulators. C. W. MARSHALL AND J. S. FORREST. Brit. 527,357, Oct. 23, 1940 (March 27, 1939).

Making spark plugs. A. C. HASTINGS, JR. U. S. 2,222,433, Nov. 19, 1940 (April 29, 1937).

Pottery-making machine. G. W. LANE AND RALPH MALARKEY. U. S. 2,224,653, Dec. 10, 1940 (Aug. 5, 1938).

Screened spark plugs. R. BOSCH GES. Brit. 528,409, Nov. 13, 1940 (May 18, 1938).

Spark plug. C. R. BUENING (Globe-Union, Inc.). U. S. 2,221,537, Nov. 12, 1940 (July 14, 1939). R. BOSCH GES. Brit. 528,410, Nov. 13, 1940 (May 18, 1938).

Water closet. E. K. H. LUNDBERG. Brit. 528,263, Nov. 6, 1940 (May 2, 1939).

Water-closet basins. E. JOHNS & CO., LTD., AND E. R. CORN. Brit. 528,110, Nov. 6, 1940 (March 14, 1939).

Equipment and Apparatus

Accuracy and other measuring properties of temperature instruments. M. F. BEHAR. *Instruments*, **13** [9] 240–42 (1940).—B. discusses the accuracy, precision, sensitivity, and readability of various types of temperature indicators and recorders. J.J.H.

Arrangement to improve the temperature distribution in laboratory (tube) furnaces. H. FLORENZ. *Aluminium*, **22** [7] 351–52 (1940).—Tube furnaces with refractory ceramic masses on which the heating element is wound have a drop of temperature at the ends for a length of about 1½ to 2 times the diameter. To improve this, another ceramic tube, about ¾ the length and about twice the diameter of the furnace tube, is placed around the latter, insulated against it by air, and surrounded by heat insulation (kieselguhr). This arrangement gives a practically uniform heat distribution over the whole length of the furnace tube; the range of uniform temperature (±5°C.) is twice as long as that in a furnace (of the same length) without the second tube. M.H.

Aspirating unit for collecting air samples. LESLIE SILVERMAN AND WESLEY B. WARDLOW. *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 682–83 (1940).—S. gives details of the construction and operation of a portable sampling unit which can be used for laboratory, field, or routine plant determinations. Illustrated. F.G.H.

Boiler feed water regulators. F. J. MATTHEWS. *Brit.*

TABLE II*

PROPERTIES OF CERAMIC INSULATORS FOR THE ELECTRICAL INDUSTRY

V.D.E.P.† specification number		Units and symbols	GROUP I Dense, predominately clay bodies			GROUP II Dense, predominately magnesium silicate bodies		
			(A) High-fired porcelain		(B) Stone properties up to discoloration	(A) Low-fired bodies	(B) Steatite	
	Method of manufacture		Extruded, cast, or press molded	Wet pressed	Pressed	Pressed	Normal	Special bodies
	Firing temperature	Seger cones °C.	13–15 1380–1435		4a–6a 1160–1200	5a–6a 1180–1200	Extruded, cast, or press molded 13–14 1380–1410	
	Significant properties		Ordinary average properties			Good rigidity, high mechanical strength	Low (loss) power factor, good rigidity, high mechanical strength	
	Uses		High- and low-voltage insulators and parts	Low-voltage insulators and insulating parts		Low-voltage insulating parts	High- and low-voltage insulators and insulating parts, especially for high frequency	
2	Water absorption	Volume (%)	0	0.1–0.5	0.4–0.8	0.1–0.8	0	
3	Volume density (specific gravity)	Gm./cm.³	2.3–2.5		2.5	2.8	2.6–2.8	
4	Tensile strength glazed	Kgm./cm.²	300–500				550–850	550–950
	Tensile strength unglazed	Kgm./cm.²	250–350					
5	Compressive strength glazed	Kgm./cm.²	4500–5500	3000–4000			8500–9500	9000–10,000
	Compressive strength unglazed	Kgm./cm.²	4000–4500	2500–3500	2500–3500	8000–9000		
6	Bending strength (modulus of rupture) glazed	Kgm./cm.²	600–1000					
	Bending strength (modulus of rupture) unglazed	Kgm./cm.²	400– 700	300–600	400–700	1000–1200	1200–1400	1400–1600
7	Resistance to impact, unglazed	Cm. kgm./cm.²	1.8–2.2	1.3–1.6	1.7–2.1	3–4	3–5	4–5
9	Linear coefficient of expansion per °C. (20° to 100°C.)	$\alpha_t \times 10^{-6}$	3.5–4.5		4.7	6.8	7.0–9.0	6.0–8.0
13	Resistance to temperature change	°C.	170					125–155
16	Puncture (dielectric) strength at 50 cycles (~)‡	Kv./mm.	30–35				20–30	30–45
17	Dielectric constant (permittivity)	ϵ	6.0 (approx.)				6.5 (approx.)	
18	Temperature coefficient of dielectric constant (between 20° and 60°C.)	$\frac{\Delta\epsilon}{\epsilon} \times 10^6$	+550 to +600 at 50 cycles				+500 to +600 at 10^6~	+120 to +160 at 10^6~
19	Dielectric (loss) power factor at 20°C. at 50~	$10^4 \times tg\,\delta$	170–250				25–30	10–15
	at 800~	$10^4 \times tg\,\delta$						8–12
	at 10^6 to 10^7~	$10^4 \times tg\,\delta$	60–120				15–20	3– 5
20	Dielectric (loss) power factor at high temperature						At 50~	At 10^6~
	60°C.	$10^4 \times tg\,\delta$	Approx. 400 at 50 cycles				Approx. 150 at 50~	40– 60 4–5
	80°C.	$10^4 \times tg\,\delta$	Approx. 600 at 50 cycles				Approx. 350 at 50~	70–120 5–6
	100°C.	$10^4 \times tg\,\delta$	Approx. 1200 at 50 cycles				Approx. 650 at 50~	120–150 6–8
21	Insulation resistance for d.c. 20°C.	Ohm × cm.	$>10^{13}$				$>10^{14}$	$>10^{15}$
	Volume resistivity d.c. or 200°C.	Ohm × cm.	10^7 –10^9		10^8	10^9	10^{16}	10^{13}
	Specific resistance a.c. 400°C.	Ohm × cm.	10^5 –10^6		10^6	10^7	10^7	10^9
	For short periods only 50~ 600°C.	Ohm × cm.	10^4 –10^5		10^5	10^5	10^6	10^7

* This table accompanies the abstract entitled "Testing specifications for ceramic electrical insulating materials," pp. 48–49.
† Verbandes Deutscher Elektrotechnischer Porzellanfabriken (Association of German Electrical Porcelain Manufacturers).
‡ ~ cycles (electric current).

TABLE II (*continued*)

PROPERTIES OF CERAMIC INSULATORS FOR THE ELECTRICAL INDUSTRY

V.D.E.P.† specification number		GROUP III Dense bodies with high content of titanium compounds			GROUP IV Clay bodies containing magnesium silicate		GROUP V Porous bodies, part clay-containing and part magnesium-containing with various additions
		(A) Vitreous rutile bodies		(B) Magnesium titanate containing bodies	(A) Dense bodies	(B) Less dense bodies	
	Method of manufacture	Various			Various		Various
	Firing temperature	11–13 1320–1380		13–15 1380–1435	13–14 1380–1410	11–14 1320–1410	6a–15 11c–1435
	Significant properties	Large dielectric constant, small (loss) power factor		Avg. dielectric constant independent of temperature, very small power factor	Small expansion, high resistance to temperature change		High heat and temperature resistance
		$\epsilon > 50$	$\epsilon < 50$				
	Uses	Condensers, especially for high frequency			Insulators and parts resistant to high temperatures	Heater elements for electric ovens	Heater elements for electric heating devices
2	Water absorption	0			0	1–5	3–15
3	Volume density (specific gravity)	3.5–3.9		3.1–3.2	2.1–2.2	2.1	1.6–2.5
4	Tensile strength {glazed / unglazed	300–800		600–700	250–350	150–250	90–160
5	Compressive strength {glazed / unglazed	3000–9000		5000–6000	3000–5000		500–2500
6	Bending strength (modulus of rupture) {glazed / unglazed	900–1500		800–1100	500–850	500–650	150–500
7	Resistance to impact, unglazed	2.5–3.3		2.6–3.2	1.8–2.2		1.0–1.9
9	Linear coefficient of expansion per °C. (20° to 100°C.)	6.0–8.0		6.0–10.0	1.1	1.2–1.7	1.8–4.8
13	Resistance to temperature change				265		Very variable, occasionally exceedingly high
16	Puncture (dielectric) strength at 50 cycles (~)‡	10–20		10–20	10–20		
17	Dielectric constant (permittivity)	60–80	30–45	12–16	5.0–5.5		
18	Temperature coefficient of dielectric constant (between 20° and 60°C.)	−650 to −750 at 10^6~	−250 to −500 at 10^6~	+30 to +50 at 10^6~	+500 to +600 at 10^6~		
19	Dielectric (loss) power factor at 20°C. at 50~ at 800~ at 10^6 to 10^7~	5–100 3–10		8–12 0.7–0.8	200 40–70		
20	Dielectric (loss) power factor at high temperature 60°C. 80°C. 100°C.	3–10 at 10^6~	5–10 at 10^6~	1.2 at 10^6~ 1.2 at 10^6~ 1.5–2.5 at 10^6~			
21	Insulation resistance Volume resistivity Specific resistance For short periods only	for d.c. 20°C. d.c. or a.c. 200°C. a.c. 400°C. 50~ 600°C.		$>10^{14}$ 10^{12} 10^8 10^6	$>10^{13}$ 10^8–10^9 10^6–10^7 10^4–10^5	 10^{10} 10^8 10^6	 10^8–10^{11} 10^7–10^9 10^6–10^8

Clayworker, **49** [580] 96 (1940).—The provision of equipment which automatically regulates the admission of feed water to boilers ensures greater safety in operating conditions and effects useful economies in the generation of steam. M. discusses these points in detail and describes how such regulators operate. R.A.H.

Calibration of thermocouples at low temperatures. RUSSELL B. SCOTT. *Jour. Research Nat. Bur. Standards*, **25** [4] 459–74 (1940); RP 1339. Price 5¢.—S. describes the apparatus and methods used at the National Bureau of Standards for the calibration of thermocouples between 0° and −190°C. A reference table for copper-constantan thermocouples is given. Curves show the deviations from the table of a number of thermocouples calibrated at the National Bureau of Standards. These curves, which represent the behavior of a number of couples from different sources, constitute the basis or a discussion of the relation between the accuracy obtainable with a copper-constantan thermocouple and the number and positions of the calibration points. R.A.H.

Capillary flowmeter. HUBERT N. ALYEA. *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 686 (1940).—Details of construction are given. Illustrated. F.G.H.

Classifications of temperature instruments can serve as practical tools. M. F. BEHAR. *Instruments*, **13** [9] 237–39 (1940).—B. discusses the following classifications of temperature instruments: (1) brief classification, (2) classification of temperature instruments by the measurement methods employed, and (3) industrial classification of temperature measuring instruments. J.J.H.

Complete photoelastic instrument. F. W. BUBB. *Jour. Optical Soc. Amer.*, **30**, 297–98 (1940).—Michelson's interferometer is adapted to provide a photograph of the isopachic fringes for any transparent plane test model under plane stress. Since the instrument may easily be converted into a polariscope without disturbing the model, a complete experimental solution for all problems of plane stress is possible. See "Isopachic...," *Ceram. Abs.*, **19** [4] 100 (1940). A.P.

CO_2 recorders—development, types, and use: I, Objective and structural considerations. D. J. BRADBURY. *Ind. Power & Fuel Economist*, **16** [179] 152–54 (1940). **II, Sarco, Simmance Abady Wright, Auto, Electroflo, and Hayes types.** *Ibid.*, [180] 172–75, 179 (1940).—Illustrated. F.G.H.

Electrically heated rotary kiln. E. P. BARRETT, W. L. BARRETT, AND P. R. PORATH. *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 684–85 (1940).—Details are given of the construction and operation of an electrically heated rotary kiln of laboratory size, 16½ in. in length and 15 in. in diameter. Illustrated. F.G.H.

Electromagnetic separator for mineral powders. R. C. EVANS. *Mineralog. Mag.*, **25** [167] 474–78 (1939).—E. describes an electromagnetic separator constructed to be (1) robust in mechanical design, (2) dustproof and easy to clean, and (3) free from trouble with electrical contacts (through the use of mercury switches). H.I.

Filter media. F. J. VAN ANTWERPEN. *Ind. Eng. Chem.*, **32** [12] 1580–84 (1940).—The use of filter cloths made of glass, rubber, wire, and resins is described and illustrated. F.G.H.

Forming clayware by hot-pressing makes new products possible. C. G. HARMAN. *Brick & Clay Record*, **94** [1] 15, 46 (1939).—The most practical method of fabrication is to bring the clay to the desired temperature in a furnace and then quickly transfer it to a press or rolls. A press was designed and built which would give the desired pressure and rapidity of action. This press was very similar to a glass press. In conducting a test, the hot clay was taken from the furnace with tongs and thrown into the mold. The mold was thrust into proper position, and the pressure was applied immediately. As soon as the pressure was released, the mold was opened and the specimen was moved to another furnace which was kept at a steady temperature of 1380°F. Success of the operation depended upon the rapid handling of the material. It was necessary to complete the pressing operation while the clay was still hot enough to yield under pressure and to place the tile in an annealing oven while it was still above 1300°F. H. gives detailed results of tests made on three types of clay. One of the most important advantages of the process is its use for the fabrication of thin units. A few 4- x 8- x ⅛-in. units were successfully formed which show promise for use as lightweight roofing, floor, or wall tile. A wide range of colors was obtained. J.J.H.

High sensitivity radiation pyrometer. N. E. DOBBINS, K. W. GEE, AND W. J. REES. *Trans. Brit. Ceram. Soc.*, **39** [8] 253–57 (1940).—By means of an arrangement whereby the image of a hot body or surface of the test piece is thrown on a photoelectric cell, the authors developed a radiation pyrometer which is claimed to have a sensitivity of between 10° and 20°C. per scale division at 2000°C. R.A.H.

Industrial thermometry. M. F. BEHAR. *Instruments*, **13** [9] 243–67 (1940).—B. discusses the mercury-in-glass, solid-expansion, pressure-spring, and resistance types of industrial thermometers. Illustrated. J.J.H.

Machine flowerpot making in France. ANON. *Brit. Clayworker*, **49** [581] 131–32 (1940).—A description is given of what a satisfactory machine should accomplish, the perfect mold, and the drying and firing of flowerpots. R.A.H.

Measuring and recording sulfur dioxide and oxygen. D. J. BRADBURY. *Ind. Power & Fuel Economist*, **16** [175] 71–74; [176] 103–107 (1940).—B. discusses the measurement and recording of sulfur dioxide and oxygen in flue gases. Illustrated. F.G.H.

Method of determining moisture content of silicate raw materials and unfinished ware. E. D. PEVZNER. *Prom. Stroitel. Materialov*, **1940**, No. 2, pp. 60–63.—The determination is conducted in a Le Châtelier-Candlot device in a manner similar to that used in specific weight determinations. P.B. & E.S.

Modern box-type enameling ovens. ANON. *Machinery* [London], **52** [1339] 282–83 (1938).—Electrically heated ovens, gas-heated ovens, and steam and water heating systems are discussed. F.G.H.

Practical hints on use of the hand Orsat apparatus. ROBERT W. ROGERS. *Nat. Engr.*, **38** [12] 455–57 (1934).—Flue-gas analysis is briefly discussed. F.G.H.

Preventing oil-engine corrosion. F. J. MATTHEWS. *Brit. Clayworker*, **49** [581] 118–19 (1940).—Adequate and suitable supplies of cooling water are vital to the satisfactory operation and long life of oil engines. M. discusses the problems encountered in the use of various soft waters for engine cooling, e.g., acidity, the danger of corrosion from water containing dissolved gases, and the wasting of the iron by the formation of the black oxide of iron from dissolved gases in the water. R.A.H.

Pyrex all-glass microelectrophoresis cell. DAVID R. RIGGS. *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 703–705 (1940).—Details of construction are given. Illustrated. F.G.H.

Simple electric furnace. KARL S. WILSON AND WALTER O. WALKER. *Ind. Eng. Chem., News Ed.*, **15** [24] 541 (1937).—Details of construction of a small laboratory furnace are given. Illustrated. F.G.H.

Simplified distinctness-of-image glossmeter. ROBERT J. MYERS. *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 678–81 (1940).—A glossmeter has been designed and constructed to measure the distinctness-of-image gloss of painted surfaces. Although the theory of the instrument is based upon the existence of minute irregularities on, in, or beneath the surface of the paint film, the data collected thus far do not prove that distinctness-of-image gloss is affected solely by the presence of such irregularities. The instrument is flexible in its application and has been found valuable in various problems dealing with a gloss denoted as distinctness-of-image gloss. Its advantages are (1) simplicity of construction, (2) simplicity of operation, and (3) capability of yielding a reproducible gloss value in numerical form. Illustrated. F.G.H.

Solar heat for industry. ARMANDO DE ARRUDA PEREIRA. *Bol. Inst. Engenharia*, **31** [152] 65–70 (1940).—One of the

most important characteristics of the sun is its power to radiate energy. It supplies 3.79×10^{33} ergs per sec. in the form of light, heat, and other ether waves to its planets, the planets and their satelites receiving only one part of 120 million, a quantity of energy not equaled anywhere on earth. This astronomic energy is regular and constant. Various instruments have been devised. Langley in 1880 invented an apparatus which registers a temperature difference of 1/100,000°C. The solar constant was established as the quantity of energy perpendicular to 1 sq. cm. per min. According to Abbott this is nearly 1.94 cal. or 81 million ergs; 1 h.p. = 735.5×10^7 ergs per sec., and 1 watt = 10 million ergs per sec. The influence of the sun is registered directly by wind and water. It has given us wood, coal, gas and oil, ores, minerals, and other "accumulated capital." The U. S. possesses underground reserves of 17 billion barrels of oil, and the total resources range between 25 and 35 billion barrels, an amount almost 30 times the yearly consumption. The yearly petroleum production in the U.S. from 1934 to 1938 was nearly 1 billion barrels; in 1939 it exceeded 1,250,000,000 barrels. At this rate, in less than a third of a century the American deposit will be exhausted. Statistics from other countries are less reliable but the deposits of the world may be exhausted within 75 years. Substitutes for fuel oil exist, however. Gasoline and oil are being abstracted from rocks rich in carbon by hydrogenation and polymerization. These products are actually competing with natural petroleum products in countries far from such resources. The U. S. possesses coal resources to assure their use and the manufacture of gasoline and oil from them for about 2000 years. Additional deposits of bituminous schists assure that the supply will not be exhausted for 3000 or 4000 years. There is no reason why solar energy should not be used to conserve our combustibles. P. gives historical data on solar mirrors from the time of the Romans and Greeks to the present. A list of substances and their reflective and absorptive powers is given and discussed, and the principle of focal reflection is explained with one illustration. P. reviews inventions by Ericsson (1868–1875), the work of William Calver in Arizona, and the solar motors of California, the Sahara, Persia, Mongolia, Mexico, and Australia. He also reviews the work of Shuman, Willsie, and Boyle (*Eng. News*, May, 1909), stating that, according to Willsie, the cost per h.p. on a 400-h.p. installation for coal would be 66¢ per ton for the thermoelectric power compared with solar electric power. To apply solar heat to clay working, S. Caetano is considering the construction of drying units with a daily capacity of 50 tons. Clays contain generally 20 to 25% moisture which must be removed prior to pulverization. The rotary drier shown reduces the moisture of 50 tons of clay to 4% in 24 hr., requiring about 300 cal. per kgm. of clay, 25 gm. of fuel oil of 12,000 cal., 37.7 gm. of imported coal of 8000 cal., or 50 gm. of local coal of 6000 cal. The apparatus is to be constructed as shown. The shredded clay enters a machine called a Tonraspler. Instead of a regular furnace, there is a chamber with a battery of coils through which steam circulates; the steam is generated from the water and vaporized through a properly constructed mirror concentrating the sun rays. A centrifugal fan exhausts the air from the heat chamber through the rotary drier in which the clay is broken up and dried in the same way as if a fuel were used. The drier may be rotated by steam obtained from the same solar heat generator. Another modification has a chamber with well-fitting insulated partitions with a double glass as receiver. In this chamber thin black metal sheets are conveniently arranged. The solar heat rays are concentrated upon the glass receiver by a system of reflecting mirrors. An exhauster moves the air over the clay to be dried. São Paulo has 180 sunny days per year for drying, and 21% of the moisture can therefore be economically removed from the clay; the stock of clay accumulated during rainy days can also be dried. This method is even more feasible in northern Brazil which has 340 days or more of bright sunshine. In case of a shortage of subsoil water, energy may be obtained from the sun without pumps and motors, and the fertility of the soil may thus be maintained. Further information on solar heat in industry may be obtained from the Secretary of the Institute of Engineers of São Paulo. T.W.GARVE

Synthetic optical crystals. H. C. KREMERS. *Ind. Eng. Chem.*, **32** [11] 1478–83 (1940).—Present-day advances in ultraviolet and infrared spectroscopy have brought about the need for more and larger optical crystalline materials than are found in nature. Lithium fluoride crystals up to 8 lb. in weight are grown. Optically similar to fluorite, lithium fluoride can effectively replace this limited natural supply. Sodium chloride crystals up to 25 lb. in weight, which are superior to natural rock salt, and potassium bromide and potassium iodide crystals for far-infrared transmission are also grown. Natural calcite of optical quality is scarce, and the increasing demand for polarizing optics has stimulated the development of the production of large single crystals of sodium nitrate. All of these optical crystals are grown from their molten salts under carefully controlled gradient and temperature. A 25-lb. crystal requires 10 days to grow and at least that long to anneal. Illustrated. F.G.H.

Unshakable foundations of temperature measurement. M. F. BEHAR. *Instruments*, **13** [9] 230–36 (1940).—B. gives a history of the development of temperature measuring and reading instruments from the time of Galileo to the present. The International Temperature Scale is described. J.J.H.

Welding of thermocouple junctions. V. M. HICKSON. *Jour. Sci. Instruments*, **17** [7] 182–86 (1940).—H. discusses the different methods for constructing thermocouple junctions and describes the apparatus for resistance butt welding and arc welding wires. 3 figures. J.L.G.

BOOKS AND SEPARATE PUBLICATIONS

Acceptance-Test Charts for Machine Tools: I. INSTITUTION OF PRODUCTION ENGINEERS, RESEARCH DEPT. Inst. of Mechanical Engineers and Inst. of Production Engineers, London, 1940. 15 pp., 6 charts. Price 5s 6d, single charts 6d each.—The charts show tests to be applied to machines, methods of testing, and tolerance, together with practical tests and tolerances. They cover center lathes, milling machines, external grinding machines, and radial drilling machines. The Schlesinger geometric tests (accuracy of the machine) and the Salmon practical tests (accuracy of work finished on the machine) are combined in a manner which helps to end the rivalry between them. The charts are available for instant use as test sheets. They ensure that a machine which is within the specified tolerances is of an accuracy to give confidence in the quality of the work produced by it. A.B.S.

Pyrometry of Solids and Surfaces. R. B. SOSMAN. American Society for Metals, Cleveland, 1940. 98 pp. Price $2.50. Reviewed in *Mech. Eng.*, **62** [12] 925 (1940).—Three lectures prepared for the American Society for Metals are presented: (1) Scientific foundations of the pyrometry of solids; (2) Pyrometry of metals by means of thermocouples; and (3) Radiational pyrometry of solids and surfaces. A brief list of references is included. F.G.H.

Temperature, Its Measurement and Control in Science and Industry. Papers presented at a symposium in New York, November, 1939, held under the auspices of the American Institute of Physics, the National Bureau of Standards, the National Research Council, and 12 scientific and technical societies, including the American Ceramic Society. Reinhold Publishing Corp., February, 1941. 1300 pp., 550 illustrations. Prepublication price until February 1, 1941, $9.00; after publication, $11.00. Reprints of the Standard Reference Tables found in the Appendix, bound in a flexible cover, may be purchased for $1.00 per copy.—Fundamental knowledge in the field of temperature and its measurement is exhaustively covered. The book comprises a collection of 125 papers by eminent engineers, metallurgists, physicists, physicians, and biologists. A thorough description of all phases of temperature technique and profound theoretical treatment

of the thermodynamics and physics which underlie the various temperature scales are given.

The scope ranges from the closest possible approach to absolute zero to the temperature of the stars and from the production and loss of heat in the body to measuring the temperature of volcanoes. Innumerable methods of precision pyrometry are described in detail. Low-temperature cancer therapy, cooling of massive concrete structures, temperature conditions in oil-well drilling, artificial fever, high-temperature arcs, molten steel pyrometry, and many more subjects of compelling interest make this an essential reference work for laboratories and libraries, as well as for all who are engaged in any phase of temperature work.

This symposium was planned with the following purposes in view: (1) coordination of the treatment of the subject of temperature in the several branches of science and engineering, (2) review of fundamental principles and a recapitulation of recent progress, (3) accumulation of contributions for a comprehensive text to be published after the Symposium, and (4) improvement of technical curricula by making the latest information available. An appendix includes standard reference tables, a glossary, and indexes.

PATENTS

Clay guns. J. Miles and H. A. Brassert & Co., Ltd. Brit. 528,576, Nov. 13, 1940 (March 30, 1939).

Color comparator. J. W. Forrest and H. W. Straat (Bausch & Lomb Optical Co.). U. S. 2,221,916, Nov. 19, 1940 (Dec. 23, 1938).

Drills for brickwork, etc. W. Coulthread. Brit. 528,524, Nov. 13, 1940 (May 5, 1939).

Electric heating element. Siemens-Schuckertwerke A.-G. Fr. 836,610, April 14, 1938.—The element consists of a heat conductor, a rod-shaped resistance, and a ceramic protecting tube. D.A.B.

Forming ceramic ware. R. E. Gould and D. A. Deaderick. U. S. 2,221,794, Nov. 19, 1940 (June 13, 1938).—In an apparatus for forming a ceramic article from fluid plastic material by casting, the improvement comprises the combination of a fluid-pervious mold with a substantially plano-convex molding surface and detachable means for maintaining a substantial amount of fluid plastic material above the surface of the mold which comprises a rigidly reinforced pneumatic ring surrounding the mold and means for readily inflating and deflating the ring.

Preparing finely comminuted oxides. Corning Glass Works. Brit. 527,855, Oct. 30, 1940 (May 14, 1938).

Kilns, Furnaces, Fuels, and Combustion

Cleaning of coal by heavy liquids. M. G. Driessen. *Engineer*, **167** [4351] 688–90; [4352] 718–20 (1939).—D. discusses the static separation of coal and dirt by heavy liquids. A new suspension washing process is described in which a large thickener is not required for regeneration of the suspension; instead, the heavy liquid is recovered by cyclone thickeners. Illustrated. See *Ceram. Abs.*, **19** [6] 146 (1940). F.G.H.

Comparative costs of different fuels. Paul R. Winston. *Nat. Engr.*, **40** [11] 514–15 (1936).—W. explains the use of a chart for making a selection of the most economical fuel to buy. F.G.H.

Composition of methane—displacements of mixtures giving maximum flame velocities. A. R. T. Denues and Wilbert J. Huff. *Jour. Amer. Chem. Soc.*, **62** [11] 3045–47 (1940).—Data showing effects of the oxygen content of atmospheres used for the combustion of methane on flame velocities and on displacements of mixtures giving maximum flame velocities are presented and briefly discussed. A new regularity between these displacements in the combustion of methane and the parameter cited has been adduced which contrasts with earlier indications for methane and complements relations derived by the writers from published data for other gases. Illustrated. F.G.H.

Discussion on "Draft in burning practice." W. S. Sells, J. G. Seanor, and L. R. Whitaker. *Brick & Clay Record*, **97** [3] 28–29; [4] 24–25 (1940); see *Ceram. Abs.*, **20** [1] 25 (1941). J.J.H.

Electric kiln for pottery firing. F. H. Norton. *Bull. Amer. Ceram. Soc.*, **19** [12] 463–64 (1940).—2 figures.

Extraction of natural and artificial coals with solvents. E. Berl and W. Koerber. *Ind. Eng. Chem.*, **32** [12] 1605–1607 (1940).—The quality and quantity of the bitumen, the material which can be extracted from natural and artificial coals with solvents, determine the technical value of these fuels. Illustrated. F.G.H.

Fuel economy in brickworks. J. Edward. *Brit. Clayworker*, **49** [581] 121–22 (1940).—Fuel economy in intermittent and other types of kilns using fire grates is discussed on the basis of (1) the furnace, (2) the flues, and (3) the chimney. R.A.H.

Fuel oil and its combustion. R. J. Bender. *Nat. Engr.*, **43** [8] 387–90 (1939).—B. considers oil burning from the "smoke prevention" viewpoint and determines which characteristics in a liquid fuel and which features in the manner in which it is burned tend to make its combustion smokeless and inoffensive. Illustrated. F.G.H.

Fuel oil and its combustion: I, Elementary facts on fuel oil. John A. Roulton. *Nat. Engr.*, **39** [6] 224–27 (1935). **II, Preheating and oil burners.** *Ibid.*, [7] 268–70; [8] 313–15. **III, Oil-fired furnaces.** *Ibid.*, [10] 395–96; [11] 438–40. **IV, Baffles for oil-fired boilers.** *Ibid.*, [12] 483–84. **V, Stacks and draft.** *Ibid.*, **40** [1] 26–28; [2] 72 (1936). **VI, Operation and control of oil-fired furnaces.** *Ibid.*, pp. 72–73; [3] 119–20; [4] 161; [5] 207–208; [7] 301–302. **VII, Computing efficiency.** *Ibid.*, pp. 302–304. **VIII, Figuring heat balance.** *Ibid.*, [8] 350–53; [9] 410, 414. F.G.H.

Heat insulation. Otto T. Koritnig. *Glashütte*, **70** [36] 474–76 (1940).—Insulation for industrial furnaces is discussed. The insulating layer is placed between the inner grog lining and the outer layer of brick, and it has been found by calculation that the layer need not be very thick to prevent heat loss through radiation and accumulation. Heat conductivity curves give a good indication of the efficiency of a substance within a definite temperature interval. Kieselguhr is the most efficient, and it can be used as a loose mass or in the form of fired block with a clay bond. At 400° its heat conductivity figure is 0.079; that of the shaped pieces is 0.120 Cal./sq. m./hr./°C. Second in efficiency is slag wool (concrete) which can be used only up to 700°. At 470° its heat conductivity figure is 0.123. Magnesia is next in either the molded form or in masses, the latter having a 3 to 8% higher insulating action than the former. The heat conductivity figure for grog at 400° is 0.59. The insulating layer seldom needs to exceed a two-brick thickness. Built-in insulation should be tested to ascertain whether the guarantee holds. The profitableness of insulation can be easily calculated: If O sq. m. is the furnace surface to be insulated, the furnace is in operation z hr. out of the 24 hr., T is the temperature of the furnace wall without insulation, t is the temperature of the production chamber, and λ is the figure for the total transfer of heat corresponding to the temperature, T, then the heat radiated in z hr., Q, = lambda $\times (T - t) \times O \times z$ Cal. If an efficiency of η% has been guaranteed for the insulation, then $\frac{\eta \times Q}{100} = m$ Cal. saved. For coal having a heating value of h Cal. and a furnace efficiency of η_1%, $\frac{m}{h \times \left(\frac{\eta_1}{100}\right)} =$ k kgm. coal saved in z hr. Insulation for apparatus is also discussed. M.V.C.

Midwestern coals. John W. Lucas. *Nat. Engr.*, **43** [9] 435–37, 442 (1939).—L. discusses the properties and general characteristics of coals in the midwestern field. Illustrated. F.G.H.

Neutral oils from coal hydrogenation. Action of sulfuric acid. Abner Eisner, M. L. Fein, and C. H. Fisher.

Ind. Eng. Chem., **32** [12] 1614–21 (1940).—Using 5-cc. samples of oil and a shaking machine, the action of sulfuric acid on cracked gasoline, a coal-tar distillate, and neutral oils produced by coal hydrogenation was studied. Sulfuric acid extractions show that aromatic hydrocarbons predominate in coal-hydrogenation oils and that the aromatic content increases with increase in molecular weight. Illustrated. F.G.H.

Operation of the single-retort underfeed stoker. W. M. PARK. *Nat. Engr.*, **39** [6] 220–23, 227 (1935). F.G.H.

Principles of combustion and flue-gas analysis. PARKER A. MOE. *Nat. Engr.*, **40** [1] 32–33; [3] 122 (1936). F.G.H.

Problems in combustion of liquid and gaseous fuels. JOHN A. HAYES. *Nat. Engr.*, **43** [4] 188–91 (1939).—H. discusses basic burner design, the operating range of pressure burners, and the various methods of atomization used in commercial practice. Emphasis is placed on the importance of proper draft and the elimination of smoke and carbon deposits. Smoke-density determinations are also discussed. Illustrated. F.G.H.

Properties of coal surfaces. G. A. BRADY AND A. W. GAUGER. *Ind. Eng. Chem.*, **32** [12] 1599–1604 (1940).—Wetting characteristics are particularly significant in the selective flotation of coal components and the separation of coal particles from liquids as well as in a study of the fundamental properties of coal. The degree of wetting, i.e., the extent to which a given liquid will spontaneously wet a solid in terms of the angle of contact, and related topics are discussed. Illustrated. F.G.H.

Purchase and use of fuel. E. WADSWORTH STONE. *Trans. Amer. Soc. Mech. Engrs.*, **62** [8] 639–50 (1940).—S. discusses the location of industry, sources of its fuel supply, available competing fuels and their relative cost, the purchaser's combustion equipment, and the method and efficiency of conversion, all of which are factors influencing the cost of power and the fuel necessary to produce it. The history of fuel production, supply, regulation, and use and the substantial improvement in combustion equipment during the last twenty years afford an interesting commentary upon the complicated problem of fuel purchase and supply. Illustrated. F.G.H.

Sensible selection of coal. CARROLL F. HARDY. *Nat. Engr.*, **43** [4] 192–93 (1939).—H. discusses the fundamental factors affecting coal selection. F.G.H.

Thermal-value nomograph for anthracite coal. D. S. DAVIS. *Ind. Eng. Chem.*, **32** [12] 1651 (1940).—Illustrated. F.G.H.

PATENT

Construction of and the art of firing muffle kilns. BONNYBRIDGE SILICA & FIRECLAY CO., LTD., AND W. MCBRYDE. Brit. 528,581, Nov. 13, 1940 (April 27, 1939).

Geology

Characteristics of a Virginia kyanite. J. P. SAWYER, JR., AND J. W. WHITTEMORE. *Bull. Amer. Ceram. Soc.*, **19** [12] 459–61 (1940).—2 figures, 3 references.

Determining the value of clay land. ANON. *Brick & Clay Record*, **94** [5] 15–16 (1939).—There are four basic conditions affecting the value of land containing a deposit of clay. Formulas are given as advisory guides for determining the value of land where (1) the deposit of clay is being used; (2) the deposit of clay is not being used but will be used beginning this year, (3) the deposit of clay is being used and the surface has a value, and (4) the deposit of clay is not being used and will not be used this year and the surface land has a value. Addition is made to a sinking fund each year. Examples for each case are worked out. J.J.H.

Gas and vapor movements in the soil: I, Diffusion of vapors through porous solids. H. L. PENMAN. *Jour. Agr. Sci.*, **30** [3] 437–61 (1940).—The dependence of the coefficient of diffusion, D, upon the porosity, S, of a granular solid was investigated experimentally. For steady state conditions, using carbon disulfide and acetone vapors, P. shows that a curve connecting D/D_o and S can be drawn which is independent of the nature of the solid, its moisture content, and, within limits, its texture. For a limited range of values of S ($0.0 < S < 0.7$), a good approximation is $D/D_o = 0.66\ S$, and over this range the diffusion coefficients are larger than those found by Buckingham for carbon dioxide. Investigation of the nonsteady state shows that the attainment of pressure equilibrium in soils is retarded by adsorption. P. suggests that Buckingham's low values for steady-state conditions can be attributed to premature observations of the diffusion rates; the steady state had probably not been attained when his measurements were made. **II, Diffusion of carbon dioxide through porous soils.** *Ibid.*, [4] 570–81.—Apparatus for measuring the rate of diffusion of carbon dioxide through granular soils is described, and the results obtained with it conform to the curve connecting D/D_o and S which was previously obtained for vapors of carbon disulfide and acetone. The equation $D/D_o = 0.66\ S$, which should replace Buckingham's equation, $D/D_o = S^2$, is applied to a discussion of soil aeration. A further application of the equation to water-vapor movement in soils is briefly discussed. P.S.D.

Gravitative selection factors in the sedimentation of sands. W. SCHEIDHAUER. *Chem. Erde*, **12**, 466–507 (1940). H.I.

Mineral content of kaolins with special consideration of colloidal size ranges. K. JASMUND. *Chem. Erde*, **12**, 508–35 (1940).—Six kaolins were tested to determine the grain-size distribution and the mineral content of the different fractions. Each sample showed a characteristic grain-size distribution curve. Amorphous material could not be shown to be present in any size fraction of any of the samples investigated. H.I.

Minerals in the clay fractions of a black cotton soil and a red earth from Hyderabad, Deccan State, India. G. NAGELSCHMIDT, A. D. DESAI, AND A. MUIR. *Jour. Agr. Sci.*, **30** [4] 639–53 (1940).—The mineral compositions of clays from a red earth and a black cotton soil occurring in close proximity in the field were determined. These soils are derived from very similar parent rocks, coarsely crystalline granite or gneiss. For both soils there is practically no variation in the mineralogical composition of the clay throughout the profile, but for any given clay there is some variation with grain size. The red clay, however, contains predominantly kaolinite or halloysite, while the black clay contains mainly beidellite, a member of the montmorillonite group. The topography appears to be the principal factor associated with this difference in minerals. The processes of weathering believed to have produced the contrasting clays are discussed with reference to experiments on the leaching of feldspar in the laboratory and on hydrothermal synthesis. P.S.D.

Petrographic and ceramic properties of Pennsylvanian shales of Illinois. RALPH E. GRIM. *Jour. Amer. Ceram. Soc.*, **24** [1] 23–28 (1941).—4 tables, 10 figures, 4 references. See "Petrology . . . ," *Ceram. Abs.*, **18** [5] 136 (1939).

Physicochemical properties of kaolinitic clay. L. LONGCHAMBON AND J. ZAJTMANN. *Bull. Soc. Franç. Minéral.*, **62** [1–3] 5–88 (1939).—Studies of pH by electrometric titration were made on several French clays in their natural state and after the removal of organic matter and acids and bases by electrodialysis. The time required to reach equilibrium increases with the amount of clay in suspension. For basic clays the pH increases and for acid clays the pH decreases with increase in concentration of the clay, becoming constant at about 5% for both acid and basic clays. In soils containing a small percentage of clay, preliminary separation of the coarse particles is necessary before pH determination. Fine particles of clay are more basic than coarse aggregates. Reasons are

given for preferring suspensions of clay in KCl solutions to those in water for pH determinations. See "Colloidal . . . ," *Ceram. Abs.*, **18** [7] 194 (1939). H.I.

Recovery of kyanite from north Georgia schist. W. B. Boyd. *Bull. Amer. Ceram. Soc.*, **19** [12] 461–63 (1940).—1 figure, 8 references.

Validity of the elutriation method in quantitative determinations of heavy minerals in sediments. W. E. Tröger. *Chem. Erde*, **12**, 419–32 (1940). H.I.

Weathering of tremolite. W. Tunn. *Chem. Erde*, **12**, 275–303 (1940).—A sample of tremolite, after being ground in an agate mortar, was separated by elutriation in methyl alcohol. The fraction < 1 μ was treated with solutions having pH values of 3.0, 5.8, and 9.0; the fraction 3 to 10 μ was treated with solutions having pH values of 3.0, 5.8, 9.0, and 11.0; and the fraction 1 to 3 μ was treated with N H_2SO_4 (pH 0.0). Analyses of the residues from these treatments showed that the longer the leaching (the greater the amount of solution used) and the lower the pH of the leaching agent, the higher is the content of SiO_2 in the residue. The residue from leaching with solutions of pH 0 was almost pure SiO_2, while that from solutions with pH 11 contained no SiO_2. H.I.

BOOKS AND SEPARATE PUBLICATIONS

Chromite Deposits of Grant County, Oregon; Preliminary Report. T. P. Thayer. *U. S. Geol. Survey Bull.*, No. 922-D (1940). Govt. Printing Office, Washington, D. C. 38 pp. Price 45¢.—With sufficiently high prices, probably 200,000 tons of concentrating ore averaging 20 and 25% of chromic oxide could be mined from explored deposits in Grant County. A geologic map of the chrome-bearing area on a scale of 1 mile to the inch and detailed geologic maps of the chromite bodies on a scale of 50 ft. to the inch are included. R.A.H.

Handbook on Witherite and Its Industrial Uses. Holmside and S. Moor Collieries and Settlingstones Mines, Ltd. 56 pp. Reviewed in *Chem. Trade Jour.*, **107**, 114 (1940).—Witherite is natural barium carbonate; almost the entire world's supply comes from two mines in the northern part of England. The addition of finely ground witherite increases the refractoriness of neutral firebrick and refractory linings made of chromite. The addition has been found particularly advantageous where the chrome ore used contains high proportions of serpentine. The addition of a small quantity of finely powdered witherite to aluminous and Portland cements is also advised. L.R.B.

Chemistry and Physics

Alumina floc; X-ray diffraction study. Harry B. Weiser, W. O. Milligan, and W. R. Purcell. *Ind. Eng. Chem.*, **32** [11] 1487–90 (1940).—Alumina floc consists of a hydrous mass of minute crystals of γ-$Al_2O_3 \cdot H_2O$ (γ-AlOOH). This has been established by X-ray diffraction and electron-diffraction studies. The size of the primary crystals in the γ-$Al_2O_3 \cdot H_2O$ floc increases with increase in the pH value of the solution from which it separates. In alkaline solution the transformation of γ-$Al_2O_3 \cdot H_2O$ to α-$Al_2O_3 \cdot 3H_2O$ is fairly rapid. At a given pH value, with different precipitants, the size of the primary crystals falls off in the following order: sodium hydroxide, ammonium hydroxide, sodium carbonate, sodium sulfide. The primary crystals of γ-$Al_2O_3 \cdot H_2O$ show a progressive increase in size on standing in contact with the mother liquor for periods of 1 to 24 hr. Under otherwise constant conditions, the primary crystals of γ-$Al_2O_3 \cdot H_2O$ increase in size with decreasing concentration of aluminum sulfate, in accordance with von Weimarn's rule and with the expected decrease in adsorption of the sulfate ion as the concentration decreases. By suitable changes in the pH value, time of aging, and concentration of aluminum sulfate, the floc of γ-$Al_2O_3 \cdot H_2O$ can be varied from primary crystals so small that the X-radiogram consists of two or three broad bands to primary crystals large enough to give well-defined lines. The use of aluminum sulfate and sodium carbonate at a pH value between 5.5 and 6.5 in the precipitation of the aluminum floc is favorable for the formation of the most highly dispersed crystals of γ-$Al_2O_3 \cdot H_2O$. Illustrated. F.G.H.

Colorimetric determination of phosphate. S. R. Dickman and R. H. Bray. *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 665–68 (1940).—A colorimetric method for phosphates is described which employs a molybdate-hydrochloric acid solution instead of a molybdate-sulfuric acid solution. This method is not affected by chlorides or by the ferric ion up to 15 p.p.m. Fading is less rapid with this method than with most methods. The method is applicable for phosphate determinations in soil fusions, hydrochloric acid extracts of soils, water analyses, oceanographic analyses, plant oxidations in which the sample is taken up in hydrochloric acid, and biological determinations. F.G.H.

Crystalline modification of alumina: I, Inversion of crystalline form of aluminum hydroxide on heating. Keiichi Akiyama. *Jour. Soc. Chem. Ind. Japan*, **42** [11] 830–32 (1939); Supp. Binding, p. 394B.—Aluminum hydroxide prepared from aluminum chloride and ammonia was heated at various temperatures and compared with the electrically fused alumina as well as with the natural corundum by means of X-ray analysis (Debye-Scherrer's method) in an attempt to show to which modification it belongs. By heating the hydrate to 1100°C., A. obtained it in the form of γ-alumina. From 1100° to 1200°C., it inverts rapidly to the α modification. Above 1200°C., the α form is held until it begins to melt. When aluminum hydroxide is heated without additions, the β form or the ζ form does not appear. The β and ζ forms cannot be obtained easily by heating or cooling the pure alumina. **II, Influence of CaO, MgO, Li_2O, Na_2O, and K_2O on the crystal inversion of alumina.** *Ibid.*, pp. 832–35; Supp. Binding, pp. 395–96B.—Calcium, magnesium, lithium, and alkali carbonate were added to γ-alumina, the CaO content being 3, 5, or 7% in each. After being heated for 2 hr. at 1700°C., the mixtures were cooled in air. With a CaO content above 5%, a distinctly different form of alumina was obtained which is almost the same as that obtained by Hansen and Brownmiller ("Studies . . .," *Ceram. Abs.*, **7** [5] 320 (1928)) by X-ray analysis. As the diffraction patterns of Ca aluminate did not appear because the amount of agent added was small, it was recognized as being the β form. The ζ form was also obtained with the addition of a little MgO, more than 2% Li_2O, or more than 3% K_2O. No Li aluminate existed but ζ-alumina was present as stated by H. B. Barlett (*Jour. Amer. Ceram. Soc.*, **15** [7] 361–64 (1932)). By this experiment, A. shows that ζ-alumina is obtained only by sintering the sample, not by crystallization from the molten state. M.T.

Determination of carbon monoxide. Pyrogallic-tannic acid method as adapted to standard gas-analysis equipment. Fred Cook. *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 661–62 (1940).—C. describes a method for the determination of carbon monoxide in concentrations of 0.10 to 0.002%. The apparatus is designed as an accessory to standard gas-analysis equipment and requires a special set of color standards in addition to the regularly available laboratory devices. The determination may be run either independently or simultaneously with another gas analysis. Illustrated. F.G.H.

Determination of crystal densities by the temperature of flotation method. Density and lattice constant of lithium fluoride. Clyde A. Hutchison and Herrick L. Johnston. *Jour. Amer. Chem. Soc.*, **62** [11] 3165–68 (1940).—The method described for determining the densities of crystals to the fifth decimal place is a combination of "temperature flotation" of small crystals with calibration of the flotation liquid by hydrostatic weighings.

By this means the density of lithium fluoride was found to be $d_{25} = 2.63905 \pm 0.0001$. F.G.H.

Determination of small amounts of beryllium in silicates. E. B. SANDELL. *Ind. Eng. Chem., Anal. Ed.*, 12 [11] 674–75 (1940).—In sodium hydroxide solution morin gives a sensitive fluorescence reaction with beryllium, which, under the proper conditions, can be made practically specific for beryllium. Its sensitivity is greater than that of the quinalizarin reaction which has been used for the determination of small amounts of beryllium in silicates. Morin was used as the reagent in the present method. The silicate sample is decomposed by fusion with sodium hydroxide, and ice is added to the cold melt. This method of decomposition has been used by Rienäcker for the detection of beryllium in silicates and for the rough estimation of the element, with quinalizarin as reagent. The mixture is filtered after disintegration of the melt, and the insoluble material is washed and re-fused with sodium hydroxide. Beryllium is then determined in aliquot portions of the two filtrates by adding morin and then comparing them with a standard series in ultraviolet light. F.G.H.

Determination of small amounts of potassium. Evaluation of cobaltinitrite precipitate using ceric sulfate. BERNARD KLEIN AND MENDEL JACOBI. *Ind. Eng. Chem., Anal. Ed.*, 12 [11] 687–88 (1940).—Potassium silver cobaltinitrite, $K_2AgCo(NO_2)_6$, is precipitated; the nitrite is liberated with hot alkali, acidified, and immediately titrated directly with ceric sulfate, using ferroin. The procedure is satisfactory for the determination of potassium in amounts ranging from 0.1 to 0.2 mg. The error does not exceed 2%. F.G.H.

Discussion of "Estimation of boron in glasses—flame test." H. E. WEBER AND R. D. JACOBSON. *Glass Ind.*, 20 [12] 464 (1939); see *Ceram. Abs.*, 17 [10] 342 (1938). A.P.

Measurement of apparent porosity. H. H. MACEY AND F. H. CLEWS. *Bull. Brit. Refrac. Research Assn.*, No. 45 (May, 1938); reprinted in *Trans. Brit. Ceram. Soc.*, 39 [9] 279–88 (1940); see *Ceram. Abs.*, 18 [8] 213 (1939). R.A.H.

Modifications in combustion micromethod for carbon and hydrogen. G. L. ROYER, A. R. NORTON, AND O. E. SUNDBERG. *Ind. Eng. Chem., Anal. Ed.*, 12 [11] 688–90 (1940).—Illustrated. F.G.H.

Potassium-sodium cobaltinitrite precipitate. REX J. ROBINSON AND JAMES D. HAUSCHILDT. *Ind. Eng. Chem., Anal. Ed.*, 12 [11] 676–77 (1940).—The composition of the potassium-sodium cobaltinitrite precipitate can vary, depending upon the conditions of precipitation (the most important being the temperature of precipitation) and the alcoholic and sodium concentrations of the precipitation medium. F.G.H.

Preparation of alumina and barium compounds from barium aluminate: II, Preparation from Tyozyo clay and barite. K. AKIYAMA, J. KAJIMA, AND H. AIBA. *Jour. Soc. Chem. Ind. Japan*, 42 [4] 250–52 (1939); Supp. Binding, pp. 145–46B.—The authors describe the preparation of several barium aluminate clinkers from such raw materials as barite, Tyozyo clay (produced in North China), and cokes by heating the mixture in a gas furnace at 1450°C. for 1 hr. and then digesting them with water or alkaline salt solution. The barite used was from the Tohoku district in Japan and was composed of $BaSO_4$ 96% and SiO_2 2.5%; Tyozyo clay consisted mainly of diasporic alumina mixed with kaolin (Al_2O_3 81 to 64%, SiO_2 3 to 12%, Fe_2O_3 3 to 1%; ignition loss 15 to 13%). Bauxites from India were examined for comparison. When the clinkers were treated with water, the amount of Al_2O_3 and BaO lixiviated was small in clinkers with a high SiO_2 content. With the alkali or alkaline salt solution (especially NaOH and NaCl), the lixiviations were better than those with water. An example is given as follows: The clinker used contained SiO_2 3.76, Al_2O_3 28.01, Fe_2O_3 3.99, and BaO 56.2%. When this sample is lixiviated with boiling water, the percentage of dissolution is Al_2O_3 74.0, BaO 60.0, and SiO_2 0.067%; the ratio of dissolved SiO_2 to dissolved Al_2O_3 is 0.09%. When the clinker is lixiviated with NaCl, the percentage of dissolution is Al_2O_3 76.4, BaO 69.8, and SiO_2 0.16%; the ratio of dissolved SiO_2 to dissolved Al_2O_3 is 0.21%. These methods are suitable for preparing Ba salts with Al_2O_3 as a by-product. For Part I see *Ceram. Abs.*, 18 [6] 167 (1939). M.T.

Reduction method for evaluation of titanium dioxide. HERMAN SKOLNIK AND WALLACE M. MCNABB. *Ind. Eng. Chem., Anal. Ed.*, 12 [11] 672–73 (1940).—An accurate volumetric method is described for the determination of titanium dioxide. Results compare favorably with those obtained by two standard gravimetric methods. The advantages include (1) elimination of the use of amalgams, (2) availability and inexpensive nature of the apparatus, and (3) ease of assembly. Illustrated. F.G.H.

Structures of complex fluorides. Barium fluosilicate and barium fluogermanate. J. L. HOARD AND W. B. VINCENT. *Jour. Amer. Chem. Soc.*, 62 [11] 3126–29 (1940).—X-ray data on the crystal structure of barium fluosilicate and barium fluogermanate are presented. Illustrated. F.G.H.

Symposium on optical methods for the study of molecular structure: I, X-ray diffraction method. B. E. WARREN. *Jour. Optical Soc. Amer.*, 30 [9] 369–73 (1940).—X-ray diffraction methods yield information about all three states of matter; their greatest contributions to molecular structure determination, however, have been in the study of molecular crystals. **II, Electronic-diffraction method.** L. R. MAXWELL. *Ibid.*, pp. 374–95.—The structures of more than 300 gas molecules were determined from electron interference phenomena. The information has been used in studies of the nature of the chemical bond and of the repulsion and attraction existing within particular molecules. A table lists the structure determinations of gas molecules by the electron-diffraction method up to the summer of 1940, covering configurations, bond angles, and interatomic distances. **III, Raman-spectra method.** G. M. MURPHY. *Ibid.*, pp. 396–404.—Results obtained for representative gases are discussed. A.P.

System lime–ferric oxide–silica. MILTON D. BURDICK. *Jour. Research Nat. Bur. Standards*, 25 [4] 475–88 (1940); RP 1340. Price 5¢.—The boundaries of the primary phase areas in a part of the ternary system lime–ferric oxide–silica have been established. The effect of ferric oxide in lowering the α-β inversion temperature is offered as evidence of a limited solid solution of ferric oxide in dicalcium silicate. The limit of this solid solution is placed at not more than 0.5% by weight of ferric oxide. No variation in the indices of refraction of the dicalcium silicate due to solid solution was noted. The presence of as little as 0.5% of ferric oxide, however, caused a slight shift of the lines in the X-ray patterns. The crystalline hydrated dicalcium silicate, $10CaO \cdot 5SiO_2 \cdot 6H_2O$, after treatment at 1350°C., could be quenched to maintain the β form of dicalcium silicate as verified by its X-ray pattern. Ferric oxide did not prevent the β-γ inversion in quenched samples prepared from calcium carbonate and silica gel. No ternary compounds were found in the portion of the system investigated. B. determined the amount of ferrous oxide developed as a result of heating preparations in several stability fields at their liquidus temperatures for 15 min.; it increased with increase of temperatures and with higher silica contents. R.A.H.

BOOK

Outlines of Methods of Chemical Analysis. G. E. F LUNDELL AND J. I. HOFFMAN. John Wiley and Sons, Inc., New York, 1938. 232 pp. Price $3.00. Reviewed in *Ind. Eng. Chem., News Ed.*, 16 [7] 201–202 (1938). F.G.H.

PATENTS

Making hydrous sodium silicates. G. R. MCDANIEL (Diamond Alkali Co.). U. S. 2,223,293, Nov. 26, 1940 (Aug. 26, 1938).—A method of preparing a stable, crystalline, hydrous sodium silicate comprises mixing reagents, at least one of which is hot, and thereby preparing a hot liquor containing approximately 1.75 to 2.25 molecular parts of sodium oxide to each molecular part of silicon dioxide and

containing an amount of water controlled to provide approximately 5 to 7 mols. water of hydration and to permit crystallization of substantially all of the liquor without evaporation of water therefrom, the temperature of the prepared hot liquor being above 100°C. and capable of effecting thermal crystallization of the liquor, without further addition of heat, when it is permitted to stand after it has been prepared but not sufficiently high to evaporate any substantial quantity of water therefrom, and causing substantially all of this liquor to crystallize to solid state by permitting it to stand without substantial reduction of the elevated temperature until crystallization is complete.

Manufacturing alkaline silicates in powder form. Floridienne J. Buttgenbach & Co. Soc. Anon. Brit. 528,374, Nov. 6, 1940 (May 5, 1938).

Manufacturing manganese dioxide. British Thomson-Houston Co., Ltd. (Tokyo Electric Co., Ltd.). Brit. 528,882, Nov. 20, 1940 (May 16, 1939).

Manufacturing solid alkali subsilicates. Pennsylvania Salt Mfg. Co. Fr. 826,770, Sept. 15, 1937. D.A.B.

Production of sodium aluminate products. Alfloc, Ltd. (Pennsylvania Salt Mfg. Co.). Brit. 527,979, Oct. 30, 1940 (April 17, 1939).

Titanium compounds and pigments starting with siliceous materials containing titanium. Titan Co. Fr. 844,360, Oct. 6, 1938. D.A.B.

Titanium oxide suspensions. I. J. Krchma (E. I. du Pont de Nemours & Co., Inc.). U. S. 2,220,966, Nov. 12, 1940 (July 16, 1938).

General

Boiler furnace design. C. H. Pesterfield. *Nat. Engr.*, **43** [3] 145–47 (1939).—P. discusses furnace width, furnace height, height of the bridge wall, and the calculation of the area which absorbs radiant heat in relation to the design of stoker- and pulverized fuel-fired furnaces. Illustrated. F.G.H.

Bureau of Mines metallurgical laboratories. R. S. Dean. *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 708–10 (1940).—Research facilities of the Bureau of Mines Experiment Station at Salt Lake City, Utah, are briefly described. Illustrated. F.G.H.

Computation of daylight factors in factory design. A. F. Dufton. *Jour. Sci. Instruments*, **17** [9] 226–27 (1940).—D. describes simple protractors which facilitate the computation of daylight factors in factory design. 4 figures. J.L.G.

Cubic yards in any conical pile. W. F. Schaphorst. *Ind. Eng. Chem., News Ed.*, **17** [20] 667 (1939).—S. presents a chart for determining the number of cubic yards in any conical pile. F.G.H.

Electricity in the pottery industry. Anon. *Ind. Power & Fuel Economist*, **16** [174] 59–61 (1940).—Eleven applications of electricity in the various stages of pottery production are briefly described and illustrated. F.G.H.

Chauncey E. Frazier. Anon. *Bull. Amer. Ceram. Soc.*, **19** [12] 478 (1940).

Industrial research progress at Armour Research Foundation, 1939–1940. Harold Vagtborg. *News Ed. (Amer. Chem. Soc.)*, **18** [21] 933–40 (1940).—Research activities in the fields of ceramics and nonmetallics are briefly reviewed. Illustrated. F.G.H.

Iron blast-furnace slag becomes important constructional material. W. H. Caruthers. *Mining & Met.*, **21** [403] 337–40 (1940).—Iron blast-furnace slag has become a standardized construction material. The slag is a nonmetallic product, consisting essentially of silicates and aluminosilicates of lime. It is an ideal material for use in bituminous road construction for city streets under heavy traffic. It has been used for roofing material, for water-bound macadam roads, in the manufacture of Portland and slag cements, as filter media, for track ballast, and in the manufacture of mineral wool and glass. C. describes the methods of processing and the use of blast-furnace slags. Specifications for the various uses are given. J.J.H.

Pneumoconiosis from mineral colors. J. Hagen. *Arch. Gewerbepath. & Gewerbehyg.*, **9**, 621–33 (1939).—Because of the wide distribution of colored minerals and their long use in technical processes, the opinion prevails in pertinent literature that inhalation of colored mineral dust is not conducive to silicosis. To show the fallacy of this opinion, H. first lists by color the seven minerals generally used, viz., white, yellow, red, green, brown, gray, and black, and their representative constituents. A detailed tabulation of their percentage composition is also given. Almost all such colored minerals contain quartz in the form of silicic acid or silicates, though in relatively low proportions. The colored minerals of industry are subject to mechanical processes such as washing, pounding, grinding, pulverizing, calcining, and mixing. The more finely they are processed, the more they disperse and scatter dust into the air. For some years in such plants, workers' complaints of respiratory diseases have been accumulating, especially in the pulverizing and mixed dust operations. Dust tests performed in these plants show that prolonged work under their generally unfavorable hygienic conditions causes severe pneumoconiotic changes. H. presents four cases in detail, showing Roentgen films of the lungs; three cases show second-grade silicosis, and the fourth case shows third-grade, or very severe, silicosis impairment. All four men had been employed in processing colored minerals for 15 to 28 years. To counteract the unfounded opinion that these materials are harmless, H. advises a vigorous campaign against the high content of atmospheric dust in such plants, especially where the pulverizing, grinding, and mixing processes take place, and recommends supervisory inspection and Roentgen examinations every two years. K.R.

Prevention of silicosis during work on sandblast units. H. Sauerteig. *Zentr. Gewerbehyg. & Unfallverhut.*, **25**, 297–305 (Dec., 1938).—In the iron and metal industries of Germany, sandblasting operations are carried on under regulations promulgated August 1, 1938, by the Insurance Assn. of these industries. A survey of silicosis among these industrial workers, conducted in 1936 and 1937, disclosed that 26.6% of 4616 workers studied had to be removed at once from the plants for severe silicosis. In certain individual plants 64% of the employees were similarly affected. S. illustrates the changes brought about in sandblast processes (as a result of the investigation and the new regulations) by a series of photographs with explanatory comment. Sandblast processes, long undisturbed in conservative routine, involved degreasings, enameling, and the resurfacing of products with various materials. They were executed by means of compressed air currents and fine sand comprising up to 80% silicic acid particles. Steps which reduce the incidence of silicosis due to old-fashioned conditions include (1) the substitution of closed booths for open sandblasting, (2) automatic manipulation instead of hand movements, and (3) the use of substitutes for quartz sand, thus removing the extreme hazard of the inhalation of silica dust. The present sandblasting procedure comprises the use of hydraulic pressure instead of compressed air (no more expensive and better), phosphoric acid solutions for cleansing operations (20% costlier), and the Bullard-Dunn electrolytic processes. The Insurance Assn. regulations provide for the transition from the old to the new apparatus and procedure, elucidate the personal hygiene measures obligatory upon the workers, and define the principles involved in the medical examinations, illustrating by a sample folder the records for every worker. Severe silicosis from sandblast operations is now considered avoidable by the association. K.R.

Regulations for the prevention of silicosis in sandblasting operators in casting cleaning plants. G. Zweiling. *Giesserei*, **27** [19] 362–65 (1940).—The use of steel grit in place of sand precludes the danger of silicosis entirely by the absence of quartz dust. It is more expensive than sand, but this is compensated for by the fact that 1 ton of steel

grit replaces 40 tons of quartz sand and can be used over again 150 to 250 times. Where steel grit cannot be used, wet blasting by means of a water jet should be employed wherever possible. If the work is done in enclosed chambers (with the pressure blowers outside) the following conditions should prevail:

Chamber content ($m.^3$)	Minimum air required ($m.^3$/min.)	Minimum change of air per min.
Up to 10	30	12 times
Over 10 to 20	120	10 "
Over 20 to 30	200	8 "
Over 30 to 50	240	6 "
Over 50 to 200	300	3 "
Over 200	600	2 "

Installations and German regulations are described. M.H.

Relative toxicity of lead and some of its compounds. L. T. FAIRHALL AND R. R. SAYERS. *U. S. Pub. Health Bull.*, No. 253, pp. 1–32 (1940).—More than 17 major industries in the U. S. utilize lead and its compounds. In 1937, more than 681,700 short tons were used. Workers are exposed to lead fumes and dust in the melting of lead; to lead carbonate, sulfate, and chromate and red lead in the pigment industries; to lead arsenate dust in the manufacture and use of insecticides; to lead silicate in the pottery industry; to litharge, red lead, and lead peroxide in storage-battery manufacture; and to the sulfide, carbonate, and oxide of lead in the milling and mining of lead ore. In 1936, the authors began the study of the relative toxicity of lead and its commonly used compounds. Toxicity by ingestion, by inhalation, and by intraperitoneal injection was investigated. More than 500 guinea pigs were required, the effects on their growth and their death rate being factors in the problem. The experimental procedure is intensively detailed, and the findings are charted or tabulated. Lead concentrations in the tissues, derived either from ingestion or inhalation, proved least in the liver, greater in the kidneys, and greatest in the bones. Toxic effects of lead and eleven of its compounds were found to be greatest from inhalation of the fumes and dust. The authors consider such findings of the highest significance for dusty trades using lead materials. Lead arsenate proved to be the most toxic substance by injection or ingestion, and lead carbonate and lead monoxide were found most toxic through inhalation. Similar toxicity, but in a lower degree, was shown by metallic lead and red lead, with such of their compounds as the arsenate, chromate, dioxide, phosphate, silicate, and sulfide. 50 references, 1 color photomicrograph, 1 X-ray photograph, 11 figures. K.R.

Roentgen research on the fine structure of the lungs in occupational silicosis. H. GÄRTNER. *Arch. Gewerbepath. & Gewerbehyg.*, 9, 634–59 (1939).—G. describes and evaluates previous Roentgen studies as initiated by Sartorius and Jötten ("Investigations . . .," *Ceram. Abs.*, **16** [4] 139 (1937)) in their 1935 researches, their wide extension in America, and further studies in Europe to determine the mineral substances in the silicotic lung. Dangerous mineral dusts, such as quartz, feldspar, sericite, asbestos, etc., give characteristic Roentgen pictures. Further comparative studies were necessary to establish identity between dusts produced in various industrial processes and those found in the lungs of workers engaged in those same industrial processes. G.'s research involved fifteen specimens of silicotic lungs and their six corresponding industrial dusts. By X-ray incandescence of the material and by the interpretation of diagrammatic lines exhibited in the material after the X-ray incandescence, resembling the lines seen in spectroscopic findings, the nature of the dust is revealed. Mixed dusts require special interpretation. The method is valuable as a clue in determining what dust or dusts cause the changes in the silicotic lung. 46 illustrations. 14 references. K.R.

Silicosis in iron-ore workers. L. E. HAMLIN. *Ind. Med.*, 9 [9] 421–41 (1940).—H. records his 10 years of experience with silicosis among 400 iron-ore workers. The 84 workers selected for special study were tabulated in three groups for comparison of results: the pre-silicotic group comprised 22 persons; the uncomplicated group (having no tubercular infection) comprised 37 persons; the complicated or infectious group comprised 25 persons. In the area studied, tuberculosis is very prevalent. Extensive efforts have been made, with the wholehearted support of the mining companies, to control the disease, but the miners and their families often stoutly resist both curative and prophylactic measures. One unique chart represents a miner's family for three generations in which both direct and collateral lines are invaded. Nine tables are given with interpretative comment. The Table of Clinical Symptoms includes 40 factors for record. Eleven X-ray films are reproduced to show the respective characteristics of the three groups of 84 workers. One unusual table shows the appearance of infection in the X-ray plate relative to the appearance of tubercular bacilli in the sputum. H. considers that serial X-rays with regular, concentrated sputum examinations and guinea pig inoculations are the most reliable and satisfactory means of diagnosing silicosis and silicotuberculosis. From his intensive and protracted studies he concludes that silicosis, uncomplicated and symptomless, is not a disabling disease. The rate of progress is very slow. Longevity in the three groups is fairly normal: 41 (60%) of the selected workers, with uncomplicated silicosis and with 27 years of underground exposure, reached the age of 55 years or over; 50 workers (58%) with complicated silicosis reached the age of 65 years. Signs and symptoms are more evident in far advanced conglomerate silicosis and silicotuberculosis, as the presence of infection increases them; this is especially true in the case of tuberculosis. K.R.

Securing satisfactory life from V-belt drives. W. M. H. *Ind. Power & Fuel Economist*, **16** [174] 56–57 (1940).—The choice of belts, pulleys, and centers is considered. F.G.H.

Skin hazards in American industry. L. SCHWARTZ. *U. S. Pub. Health Bull.*, No. 249, pp. 1–99 (1939).—S. reports on skin hazards in eleven American industries: citrus fruit; pulp and paper; cigars; acids; organic solvents; chromic acid and chromates; iron and steel; paints, varnishes, and lacquers; photography, photoengraving, lithography, printing, typewriting, and hectographing; glass; and explosives. The site, character, and prevalence of the dermatitis with results of tests, when given, the industrial processes in which the skin injury develops, and preventive measures in use or advised are presented. Pertinent literature is reviewed in the case of unsettled problems or varying opinions. In the larger subjects, e.g., the manufacture of acids, the chemical facts involved are concisely summarized. At least one illustration of dermatitis in each industry is presented, some being in color. A special bibliography is appended for every industry considered. K.R.

Studying the combustion process in boiler furnaces. JOHN M. DRABELLE. *Nat. Engr.*, **43** [4] 194–95, 197 (1939).—D. discusses the use of color movies in the study of combustion conditions within boiler furnaces. F.G.H.

Synthetic bonded steel molding sands. C. W. BRIGGS AND R. E. MOREY. *Trans. Amer. Foundrymen's Assn.*, **47**, 653–724 (1939).—From a simple sand mix consisting of washed silica sand, bentonite, and water, it is possible to prepare synthetic green sands, synthetic dry sands, and air-dried sands with excellent properties. The synthetic dry sand is prepared by merely oven-drying the green-sand molds. The addition of organic binders to green sand is studied in detail. H.E.S.

Useful expansion chart. W. F. SCHAPHORST. *Ind. Eng. Chem., News Ed.*, **17** [24] 790 (1939).—S. presents a chart for determining the expansion in piping, rods, tubes, etc., for any ordinary temperature difference. F.G.H.

Wide-range cylindrical tank chart. W. F. SCHAPHORST. *Ind. Eng. Chem., News Ed.*, **15** [17] 396 (1937).—A chart is presented for determining the number of cubic feet in any cylindrical tank from 1 to 200 ft. in diameter

and 1 to 300 ft. in height. The capacities vary from 2 to 10 million cu. ft. Illustrated. F.G.H.

BOOKS AND SEPARATE PUBLICATIONS

Dictionary of Occupational Titles: I, Definitions of Titles. U. S. Department of Labor, Washington, 1939. 1287 pp. Price $2.00.—This work represents the last major result of 5 years of occupational research by the U. S. Employment Service. The material on which the book is based was gathered from 55,000 job-analysis schedules in 15 states. In addition to the job title or titles, each definition includes an "industrial designation" indicating the type of business or industry with which the job is associated, an occupational code number identifying the job for statistical use, etc., by public employment offices, and a digest of the duties and responsibilities of the job. This code will be of eminent usefulness in making industrial hygiene surveys in which an occupational analysis is included. Many of the terms appear odd to the uninitiated, e.g., a screen ape is a screener of coal, a cat skinner operates a tractor, a pulpit man works in a steel mill charging and discharging a furnace, and a zoogler loads and unloads sleds or drays used to skid logs. The dictionary is also useful in differentiating between two jobs with the same title, e.g., a bulldozer operator may drive a tractor-like grading machine, bend or shape metal on a forging press, or form heads on rivets in structural steel work. F.S.M.

Dust Hazard in the Foundry Industry of Borderline Character. LEONARD GREENBURG. *Amer. Foundrymen's Assn., Management Series*, No. 5, *Rept.* No. 38-35, 36 pp. (1938).—Statistical tables demonstrate the manner in which the problem was approached and the degree of care given to the analysis. The relation of plant size to total employment in industry is given. The X-ray procedure and findings are shown. The distribution of the workers examined and the determination of the effect of previous employment are also given. A discussion on fibrosis, silicosis, and tuberculosis is included. H.E.S.

List of American Standards. American Standards Assn., Jan. 15, 1940. 12 pp.—An index is presented to standards established under the auspices of the American Standards Assn. The standards are classified according to industry and subject. Recent standards include Z 12.10-1940 (75¢), use of inert gas for fire and explosion prevention, etc.; K22-1939 (25¢), zinc oxide pigment; K29-1939 (25¢), Prussian blue; K24-1939 (25¢), red lead pigment; K31-1939 (25¢), specific-gravity measurement of pigments; K45-1939 (25¢), titanium dioxide pigment. A.G.S.

Medicolegal Phases of Occupational Diseases. C. O. SAPPINGTON. Industrial Health Book Co., Chicago, 1939. 400 pp. Price $2.75. Reviewed in *Foundry*, **67** [10] 82 (1939). F.G.H.

Stoker Handbook. H. D. AIRESMAN. J. B. Lippincott Co. 200 pp. Price 15s. Reviewed in *Ind. Power & Fuel Economist*, **16** [174] 62 (1940). F.G.H.

Twenty Years' Survey of the Use of Sheathed Explosives in Belgium. AD. BREYRE. *U. S. Bur. Mines Repts. Investigations*, No. 3530, 10 pp. Free.—B. describes the development in Belgium of the use of sheathed explosives, the manner in which difficulties encountered in their manufacture have been overcome, and the types of sheathing that have survived. The different forms of sheathing adopted by other countries are also mentioned. R.A.H.

Wetting and Detergency. Scientific and Technical Aspects. Foreword by W. CLAYTON. A. Harvey, London, 1937. 210 pp. Price 15s 6d. Reviewed in *Ind. Eng. Chem., News Ed.*, **15** [18] 421 (1937).—Twenty papers are discussed. These were presented at a symposium held in London, February, 1937, under the auspices of the British Section of the International Society of Leather Trades' Chemists. DeWalle discusses wetting and deflocculation. F.G.H.

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